

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Microemulsion Formation

The experimental data of microemulsion formations are shown in Appendix A. For microemulsion formation with motor oil, a mixture of 2 wt% Dowfax 8390, 3 wt% AOT and 2 wt% Span 80 was used as a base condition in this study. As known, types of surfactants can affect the microemulsion system. According to the structure of Dowfax 8390, it has two hydrophilic head groups, so that it is more hydrophilic and prefers to solubilize in a water phase rather than in an oil phase. It will create the dispersion of oil droplets in a continuous water phase as known as a Winsor Type I microemulsion. In contrast, Span 80, having a very low HLB value, so it is a highly lipophilic surfactant leading to solubilize in an oil phase more than a water phase. Hence, a water in oil microemulsion, Winsor Type II microemulsion is formed.

From the difference in the properties of solubilization of these two surfactants, another type of surfactant is needed for microemulsion formation with a very hydrophobic oil like motor oil. AOT, an anionic hydrophobic surfactant, was used as a linker of these two surfactants to enhance the solubilization of both motor oil and water to facilitate the formation of Winsor Type III microemulsions.

4.1.1 Effect of AOT Concentration

In order to observe the effect of AOT concentration on microemulsion formation with motor oil, both Dowfax 8390 concentration and Span 80 concentration were fixed at 2 wt%. Then an AOT concentration was varied from 3 wt% to 5 wt%. From Figure 4.1, as AOT concentration increases, the formation of Winsor Type III microemulsion appears at a slightly lower salinity and the volume fraction of the middle phase is also increased. Increasing surfactant concentration is known to be one method for promoting phase transformation (Bourrel and Schechter, 1988).

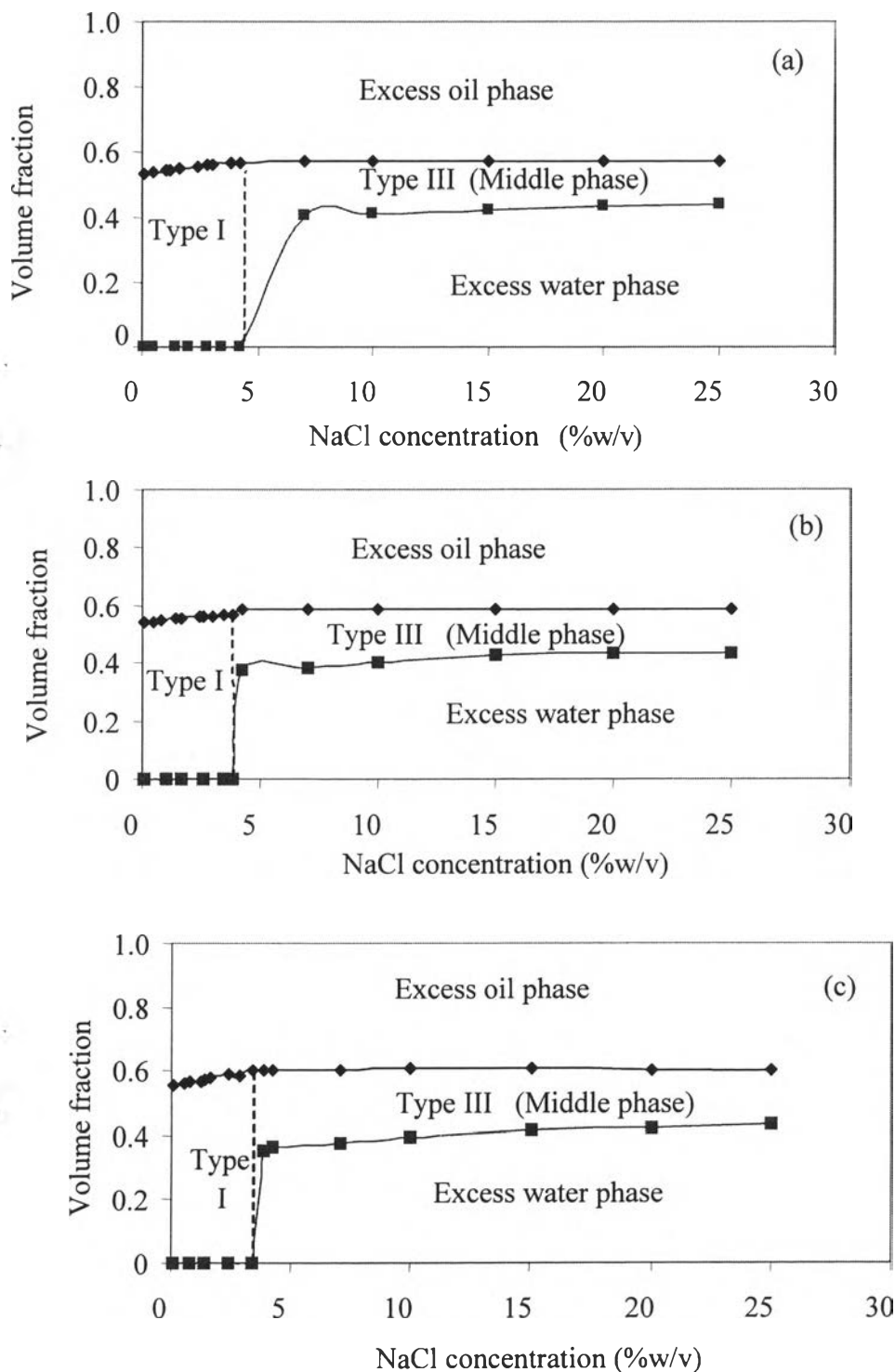


Figure 4.1 Volume fraction as a function of NaCl concentration with different AOT concentrations and at an oil to water volumetric ratio of 1 to 1, (a) 2wt% Dowfax 8390, 3wt% AOT and 2wt% Span 80, (b) 2wt% Dowfax 8390, 4wt% AOT and 2wt% Span 80 and (c) 2wt% Dowfax 8390, 5wt% AOT and 2wt% Span 80.

The result can be explained that according to a quite low HLB value of AOT, increasing AOT concentration leads to decreasing HLB value of the mixed surfactant system. The lower HLB value directly promotes phase transformation from Winsor Type I microemulsion to Winsor Type III microemulsions as shown in the phase diagram (Figure 4.1). The formulation of 2wt% Dowfax 8390, 5wt% AOT and 2wt% Span 80 was selected for further study since it can form a Winsor Type III microemulsion (The middle phase) at the lowest salinity at 4 wt%.

4.1.2 Effect of Span 80 Concentration

In order to study the effect of Span 80 concentration of the mixed surfactant system on microemulsion formation, the Dowfax 8390 concentration was fixed at 2wt% and the AOT concentration was fixed at 5wt% while the Span 80 concentration was varied from 2 to 5 wt%. Figure 4.2 shows the effect of Span 80 concentration on microemulsion formation with motor oil at different salinities. As the Span 80 concentration increased, the middle phase microemulsion was found at a lower salinity as well as a larger volume fraction of the middle phase. It can be explained by the same reason of the effect of AOT concentration because Span 80, a nonionic surfactant, which has a very low HLB value. Therefore, the HLB value of the mixed surfactant system is lowered with increasing Span 80 concentration. Hence, the system is simply forced to shift from Winsor Type I to Winsor Type III microemulsions as increasing Span 80 concentration.

4.1.3 Effect of Dowfax 8390 Concentration

To observe the effect of Dowfax 8390 concentration on microemulsion formation under the mixed surfactant system, the Dowfax 8390 concentration was varied from 1.5 to 3 wt% while the concentrations of AOT and Span 80 were fixed constant at 5 wt%. Figure 4.3 illustrates the phase behavior as a function of salinity at different Dowfax 8390 concentrations. With increasing Dowfax 8390 concentration, the formation of middle phase, a Winsor's type III microemulsion appeared at a higher salinity. A HLB value of the studied system is increased with increasing Dowfax 8390 concentration because of a very high HLB value of Dowfax 8390. As a result, the system becomes more hydrophilicity and so

it is likely, oil droplets can penetrate and disperse in the water phase known as Winsor Type I microemulsion.

Consequently, 1.5wt% Dowfax 8390, 5wt% AOT and 5wt% Span80 were selected as a formulation for detergency tests since it can form a middle phase microemulsion at the lowest salinity (2.833 wt%). As known, the detergency efficiency is related to an ultralow interfacial tension (10^{-2} - 10^{-3} mN/m) which is obtained under the presence of a Winsor Type III microemulsion.

4.2 Solubilization in Mixed Surfactant System

The effect of salt on microemulsion formation was studied by adding salt in the system is known as salinity scan. Salinity scan results of the motor oil system with different formulations are presented in Figures 4.1-4.3. For any given composition of the mixed surfactants with low salinity, the system exhibits an oil in water microemulsion or Winsor Type I microemulsion. With increasing salinity, the 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 surfactants moving out from the water phase to the oil phase. As a result, adding salt will promote the formation of middle phase microemulsion since NaCl 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. Consequently, more oil can be solubilized into the inner core of micelles resulting in changing the structure of micelles from spherical to bicontinuous structure, causing a shift from a Winsor Type I microemulsion to a Winsor Type III microemulsion. Normally, at very high NaCl concentrations, transformation from a Winsor Type III to a Winsor Type II microemulsion should occurs since more surfactants are forced to move from the aqueous phase as well as the middle phase to the oil phase which enhances the formation of an water in oil microemulsion. However, under the studied conditions, a Winsor Type II microemulsion could not be observed because of the high hydrophobicity of motor oil.

The unique properties of microemulsion are not only to have an ultralow interfacial tension but also to have a high solubilization capacity. The solubilization

is defined as a volume of either oil or water dissolved per unit mass of surfactants. The solubilization parameter as a function of salinity at different compositions of mixed surfactants is shown in Figures 4.4-4.6. In the region of Winsor Type I microemulsion, the volume of oil dissolved in the aqueous micellar phase was very small but the solubility parameter of water was very high. With increasing electrolyte concentration, the solubilization of oil (SP_o) was found to increase slightly. For Winsor Type I microemulsion system, very little water presents in the excess oil phase and virtually all water is in the aqueous micellar phase. The SP_w value is therefore relatively constant as long as Winsor Type I exists. When the middle phase microemulsion is formed, both water and oil will be moved into the middle phase since most surfactant molecules present in the middle phase. Hence, the value of SP_w decreases substantially but the value of SP_o increases gradually with increasing salinity. The NaCl concentration at the interception of SP_o and SP_w is classified as the optimum salinity. At this point, the solubilization parameters of oil and water are equal. As expected, the optimum salinity of this studied system was found in the Winsor Type III region. It confirms that the formation of Winsor Type III can enhance the solubilization of both oil and water.

As can be seen in Figure 4.4, the optimum salinity decreases with increasing AOT concentration since adding AOT reduces a HLB of this system leading to lowering salinity required to shift the system from Winsor Type I to Winsor Type III. With adding Span 80, as shown in Figure 4.5, the optimum salinity decreases, that can be explained by the same reason as adding AOT. In case of Dowfax 8390, the optimum salinity increases with increasing Dowfax 8390 concentration because adding Dowfax 8390 increases a HLB of this system. As a result, a higher salinity is required to form middle phase microemulsion as shown in Figure 4.6.

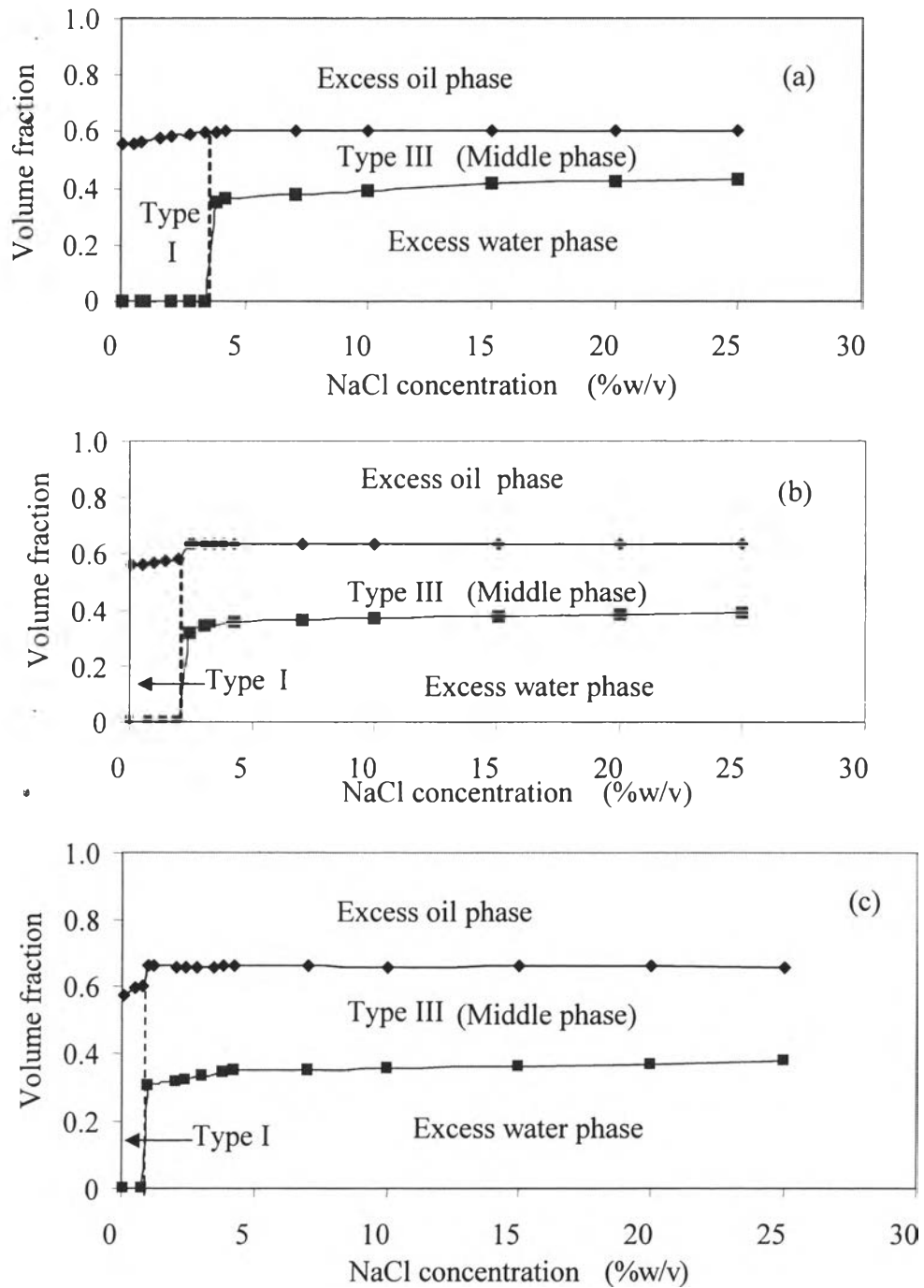


Figure 4.2 Volume fraction as a function of NaCl concentration at different Span80 concentrations and at an oil to water volumetric ratio of 1 to 1, (a) 2wt% Dowfax 8390, 5wt% AOT and 2wt% Span80, (b) 2wt% Dowfax 8390, 5wt% AOT, 4wt% Span 80 and (c) 2wt% Dowfax 8390, 5wt% AOT and 5wt% Span 80.

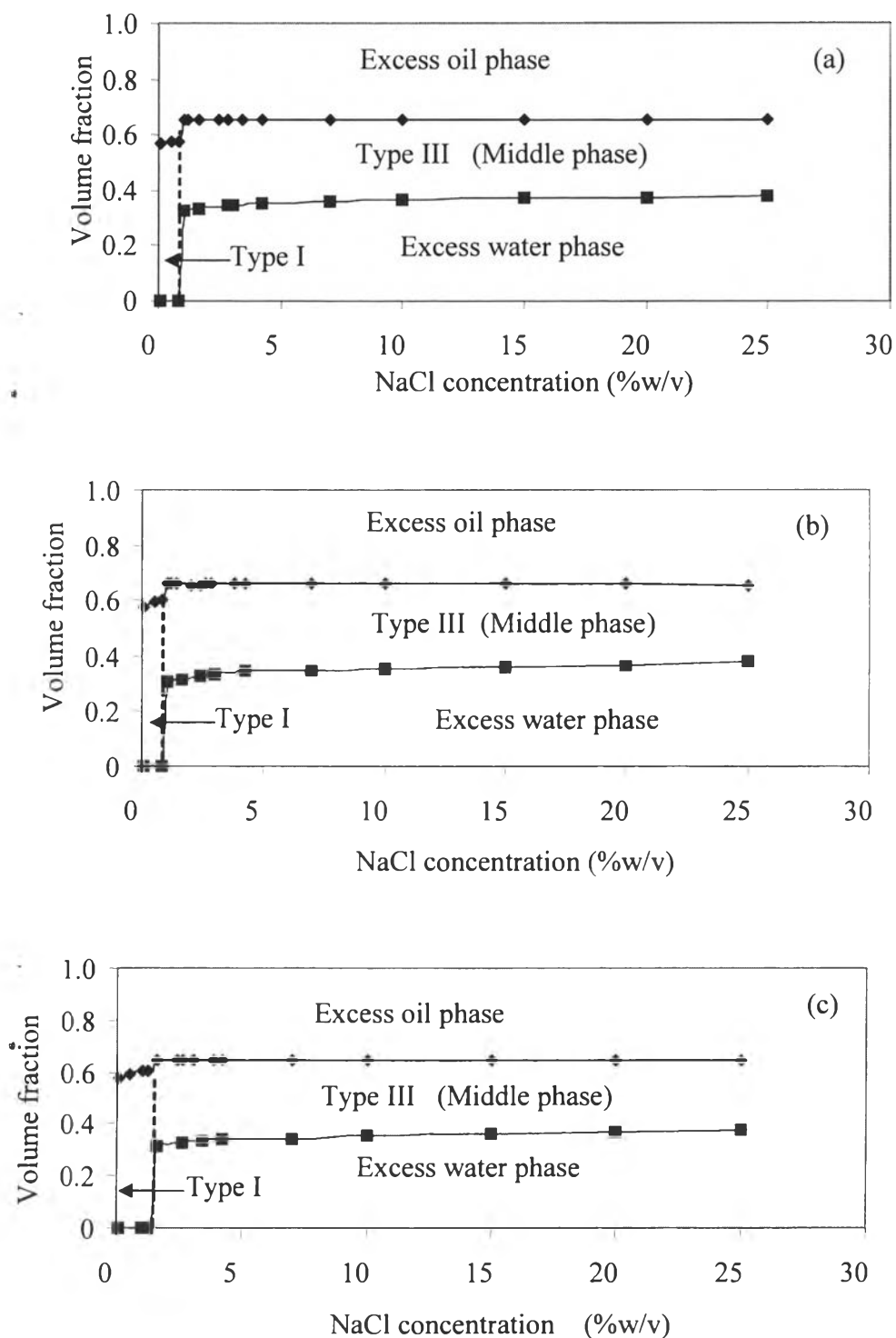


Figure 4.3 Volume fraction as a function of NaCl concentration at different Dowfax 8390 concentrations and an oil to water volumetric ratio of 1 to 1, (a) 1.5wt% Dowfax 8390, 5wt% AOT and 5wt% Span80, (b) 2wt% Dowfax 8390, 5wt% AOT, and 5wt% Span80, (c) 3wt% Dowfax 8390, 5wt% AOT and 5wt% Span 80.

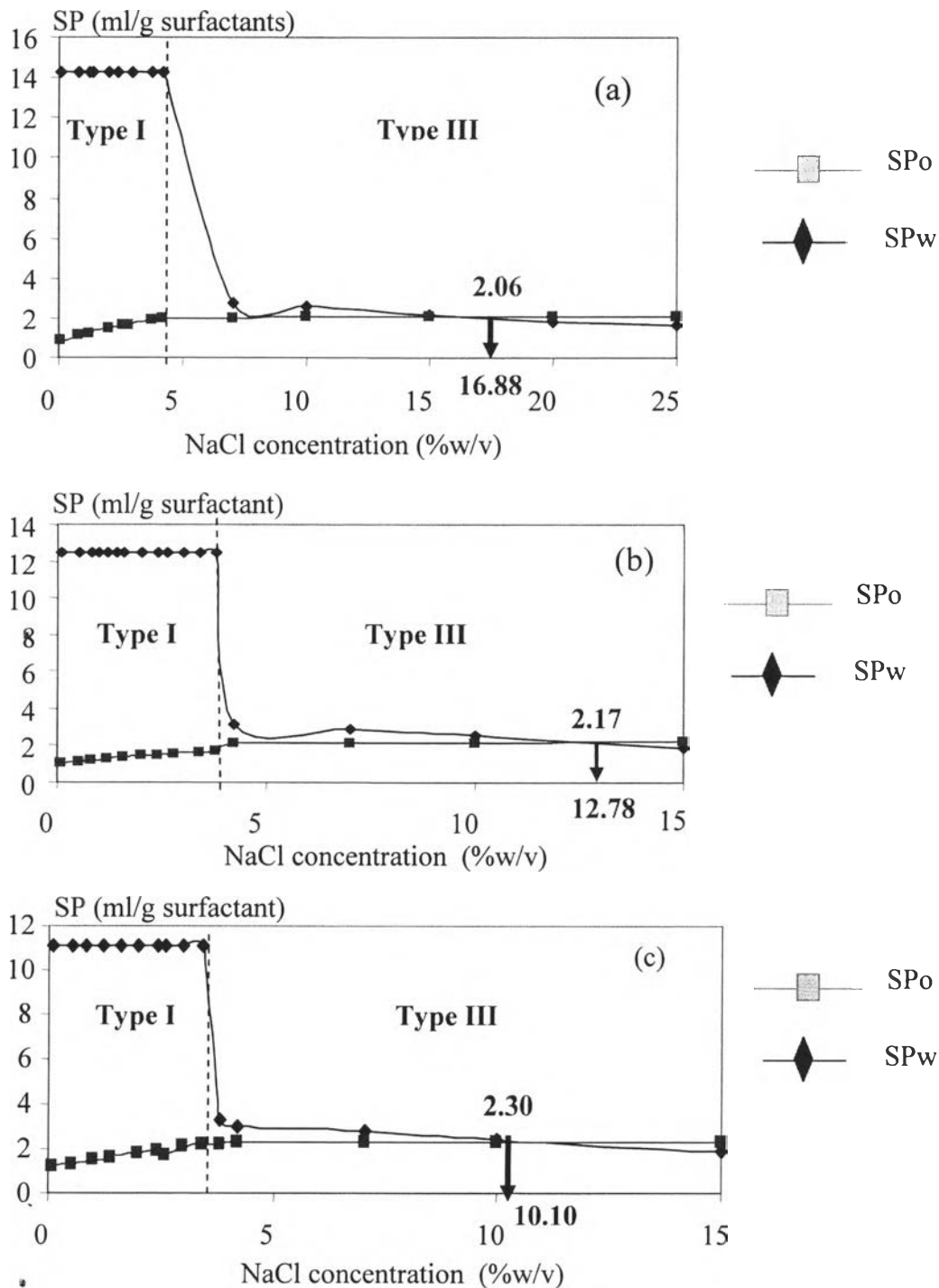


Figure 4.4 Solubilization parameter as a function of NaCl concentration at different AOT concentrations and at an oil to water volumetric ratio of 1 to 1, (a) 2wt% Dowfax8390, 3wt% AOT and 2wt% Span80, (b) 2wt% Dowfax8390, 4wt% AOT and 2wt% Span80, (c) 2wt% Dowfax8390, 5wt% AOT and 2wt% Span80.

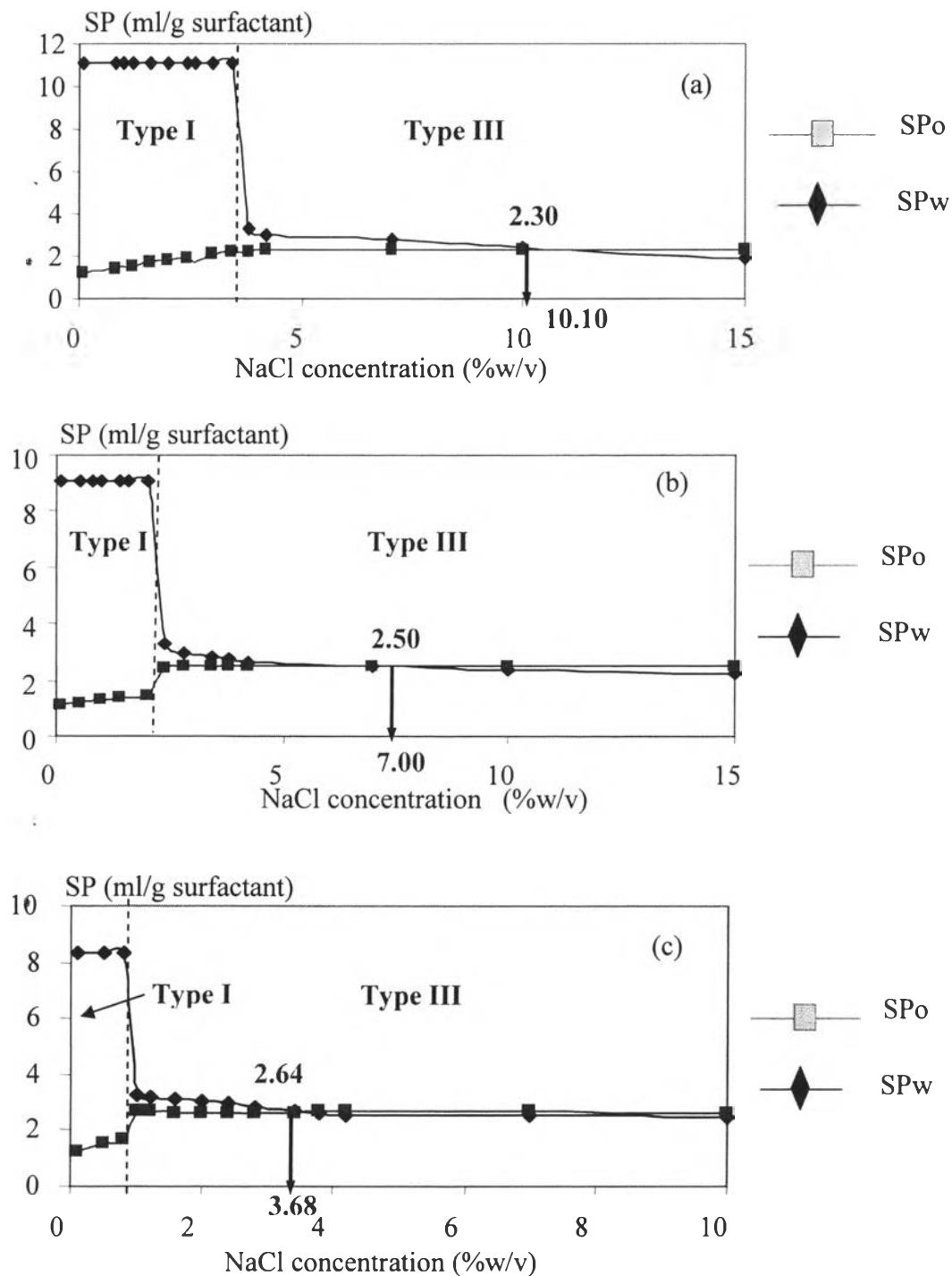


Figure 4.5 Solubilization parameter as a function of NaCl concentration at different Span80 concentrations and at an oil to water volumetric ratio of 1 to 1, (a) 2wt% Dowfax8390, 5wt% AOT and 2wt% Span80, (b) 2wt% Dowfax8390, 5wt% AOT and 4wt% Span80, (c) 2wt% Dowfax8390, 5wt% AOT and 5wt% Span80.

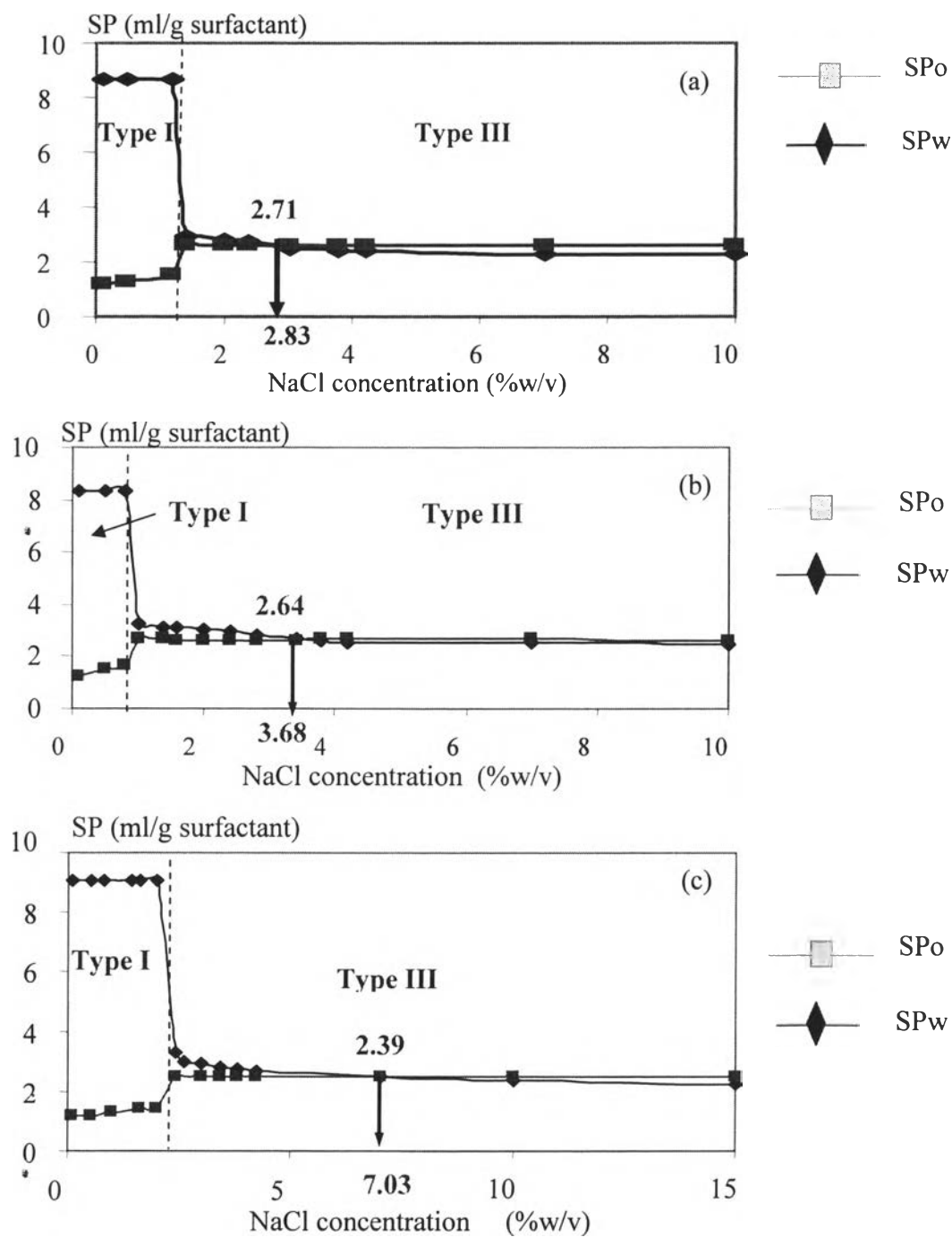


Figure 4.6 Solubilization parameter as a function of NaCl concentration at different surfactant formulations at the oil to water volumetric ratio of 1 to 1, (a) 1.5wt% Dowfax8390, 5wt% AOT and 5wt% Span80, (b) 2wt% Dowfax8390, 5wt% AOT and 5wt% Span80, (c) 3wt% Dowfax8390, 5wt% AOT and 5wt% Span80.

As mentioned before, the interception of SP_w and SP_o is classified as the optimum salinity (S^*) and the solubilization parameter at this point is called the optimum solubilization parameter (SP^*). The graphs of the solubilization parameters as a function of salinity at different mixed surfactant concentrations are shown in Figures 4.4-4.6. The solubilization parameter of the system can be expressed by the Winsor's R-ratio in terms of interaction energies as following (Rosen, 1988) :

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}} \quad (4.1)$$

where A_{CO} is the interaction (per unit interfacial tension area) between the surfactant and oil, A_{CW} is the interaction between the surfactant and the aqueous phase, L and H refer to lipophilic and hydrophilic, and A_{LL} and A_{HH} are self-interaction of lipophilic and hydrophilic portion of the surfactant, respectively. The parameter A_{WW} and A_{OO} are the self-interaction in the water phase and oil phase, respectively. The numerator of the equation represents the net interaction of the lipophilic portion of the surfactant at the interface, and the denominator represents the hydrophilic part of the interface. From Equation 4.1, to increase solubilization, both the numerator or the net interaction energy of lipophilic portion and the denominator or the net of interaction energy of the hydrophilic portion have to be increased.

For variation of AOT concentration, as shown in Figure 4.4, the optimum salinity (S^*) decreases but the optimum solubilization parameter (SP^*) increases with increasing AOT concentration. Because a system with a lower optimum salinity has a lower cohesive energies in water region (A_{CW}), the SP^* of the system will simply increase.

For variation of Span 80 concentration as shown in Figure 4.5, the optimum salinity (S^*) decreases but the optimum solubilization parameter (SP^*) increases with increasing Span80 concentration. The result can be explained by the same reason as AOT.

For variation of Dowfax 8390 concentration as shown in Figure 4.6, the optimum salinity (S^*) increases but the optimum solubilization parameter decreases (SP^*) with increasing Dowfax 8390 concentration. From the Winsor R-ratio

concept, the system with a higher salinity has a lower cohesive energies in water region (A_{CW}) resulting in reducing the SP^* of the system.

4.3 Interfacial Tension at the Optimum Region

Interfacial tension between oil and water is related to the free energy difference of the interfacial film at the planar interface separating the bulk phase and the curved interface of the microemulsion droplet. The microstructure of the middle phase is considered to be bicontinuous phase (Acosta *et al.*, 2003) and as a consequence, its curvature is almost planar. Hence, the difference in free energy is very low, resulting in an ultralow interfacial tension value. In this study, the measurement of interfacial tension was done in the region of Winsor Type III microemulsion by measuring the interfacial tension of the excess oil phase and the middle phase ($\gamma_{o/m}$) and the interfacial tension of the excess water phase and the middle phase ($\gamma_{w/m}$).

Figure 4.7 shows the relationship between interfacial tension and NaCl concentration with the formulation of 1.5wt% Dowfax 8390, 5wt% AOT and 5wt% Span 80 to form microemulsion with motor oil. It was found that with increasing salinity, the interfacial tension between the excess water and the middle phase increased but the interfacial tensions between the excess oil and the middle phase decreased. As known, the interception of these interfacial tension is the optimum salinity. As expected, the minimum interfacial tension (10^{-2} to 10^{-3} mN/m) was found at the optimum salinity. Therefore, this formulation at the optimum salinity with the ultralow interfacial tension, it is considered to be in the useful range for detergency application (Cates *et al.*, 1988).

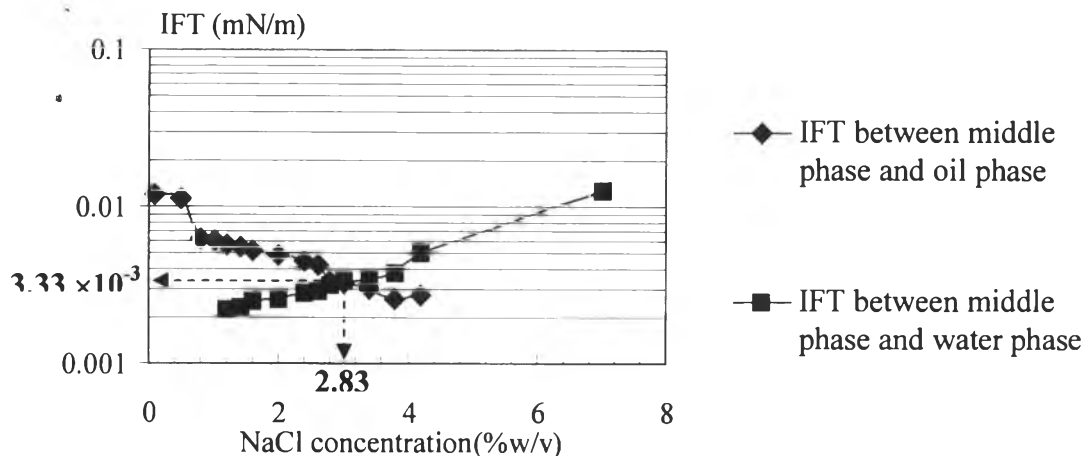


Figure 4.7 The relationship between the interfacial tension and NaCl concentration with the formulation of 1.5wt% Dowfax 8390, 5wt% AOT and 5wt% Span 80 to form microemulsion with motor oil.

4.4 Effect of Oil to Surfactant Solution Ratio on Interfacial Tension

For the phase behavior study, the oil to surfactant solution ratio was fixed constant at unity because of the simplicity in evaluating the results. As being realized in the real application of detergency, an oil to surfactant solution ratio is generally be less than one but not one to one that was used in the phase study. As known, interfacial tension is one of the most influencing parameters involving the detergency performance. Therefore, the interfacial tensions of the microemulsion systems with the selected formulation, 1.5wt% Dowfax 8390, 5wt% AOT and 5wt% Span 80 at different oil to surfactant solution ratios were measured. As shown in Figure 4.8, the value of the interfacial tension of all three ratios of oil to surfactant solution are ultralow at the optimum salinity. These three ratios of oil to surfactant solution were found to have the same optimum salinity. Hence, this formulation was selected to use in the further study in detergency experiment.

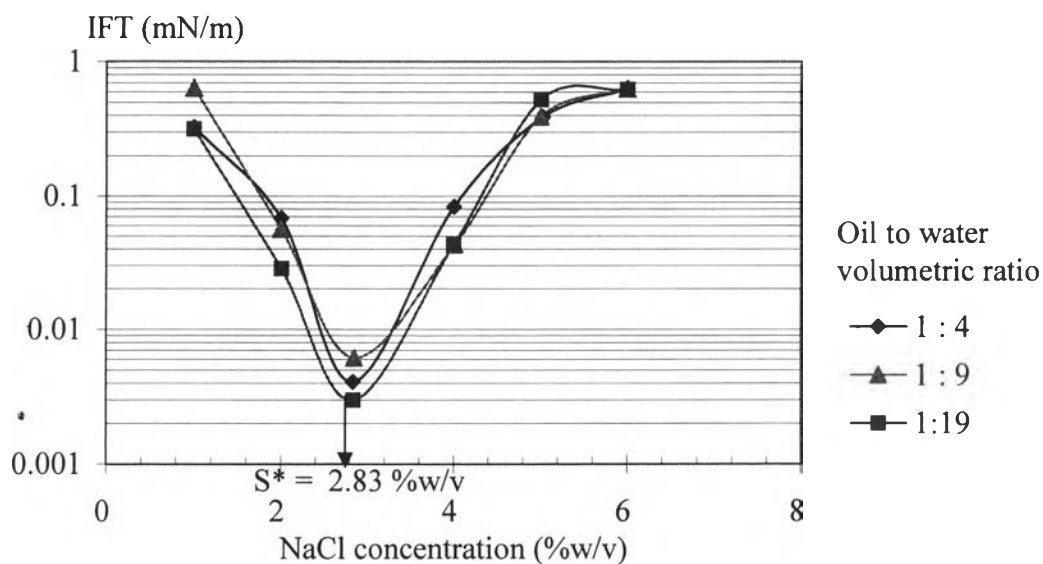


Figure 4.8 Interfacial tension as a function of salinity at different oil to washing solution volumetric ratios using the studied formulation, 1.5wt% Dowfax 8390, 5wt% AOT and 5wt% Span 80.

4.5 Detergency Performance

The experimental data and calculation methods of the detergency experiment are shown in Appendix B. The analytical methods of each component are shown in Appendix C. The detergency performance experiment is determined by two parameters; % detergency and % oil removal. Moreover, the dynamic interfacial tension is correlated to the detergency performance in order to gain a better insight about oily soil removal mechanism during detergency process.

4.5.1 Effect of Surfactant Concentration on Detergency Performance

According to the results of the phase study, a formulation of 1.5wt% Dowfax 8390, 5wt% AOT and 5wt% Span 80 at the optimum salinity 2.83 %w/v was selected for detergency experiment. Generally, percentage of liquid detergent is usually recommended at around 0.6 to 1.2 % in the washing solution or around 0.3 to 0.8 % active surfactant for detergency application (Jakobi and Löhr, 1987). For this study, the total active concentration refers to the wt% of the total surfactants in the

solution. Figure 4.9 shows the % detergency as a function of active surfactant concentration for these three types of fabrics. Under the studied conditions with the selected formulation, the % detergency increased with increasing active surfactant concentration and the system reached the plateau at around 0.1 % active surfactant for all three types of fabrics. Moreover, for any given active surfactant concentration, % detergency on pure cotton was slightly higher than those on the other two types of fabrics and the lowest % detergency was found on the pure polyester.

Another parameter used to express the detergency performance is oil removal as shown in Figure 4.10. The results show a good consistency between oil removal and % detergency. For any given active surfactant concentration, the oil removal on cotton was the highest while that on pure polyester was the lowest. Based upon the results of the detergency experiments, an optimum active surfactant of 0.1 % of the studied formulation is recommended for household application for all three types of fabrics. The use of the studied formulation at the optimum active surfactant concentration of 0.1 % could give high oil removals of 83.7%, 82.6% and 78% on cotton, polyester/cotton blend and polyester, respectively. As expected, the detergency performance of cotton was the highest level and it followed by polyester/cotton blend and polyester.

The results can be explained by the fabric nature. As known, a hydrophobic oil tends to adhere strongly on the nonpolar substrate. Therefore, it is more difficult to remove oily soil from polyester than from cotton which agrees with the results of Chi (1999). In addition, this finding coincides with that of Kissa (1971), who found that soil retention measured by a gravimetric method was lower on cellulosic fabrics and cellulosic blends than those on synthetics. Because of the high viscosity of aqueous emulsions formed by motor oil and the washing solution, roll-up mechanism is not a single mechanism for oil removal on hydrophobic fibers where the oil removal process could be completed by introducing mechanical shear. The mechanisms for oil removal will be for the discussed more in detail later.

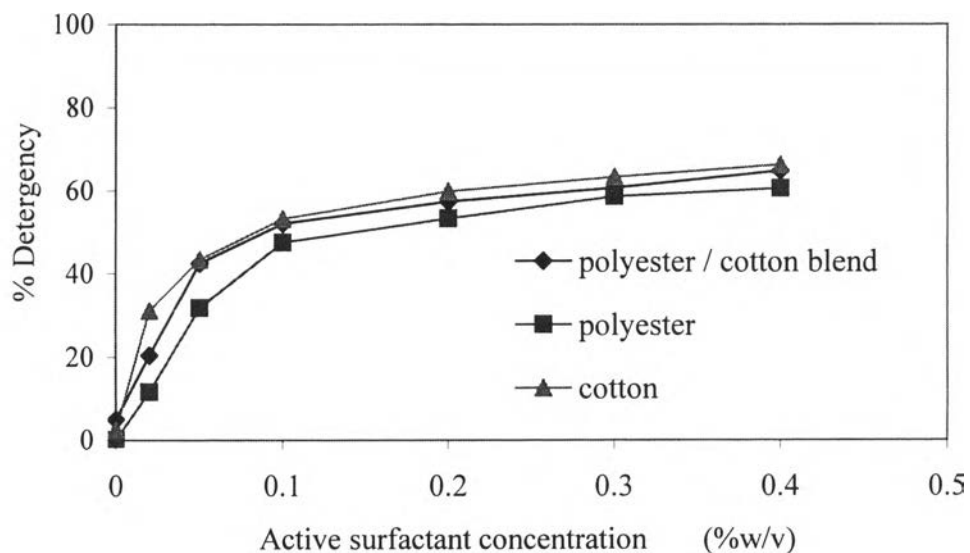


Figure 4.9 The effect of active surfactant concentration on % detergency on three types of fabrics at the optimum salinity (2.83 wt%) with the selected formulation.

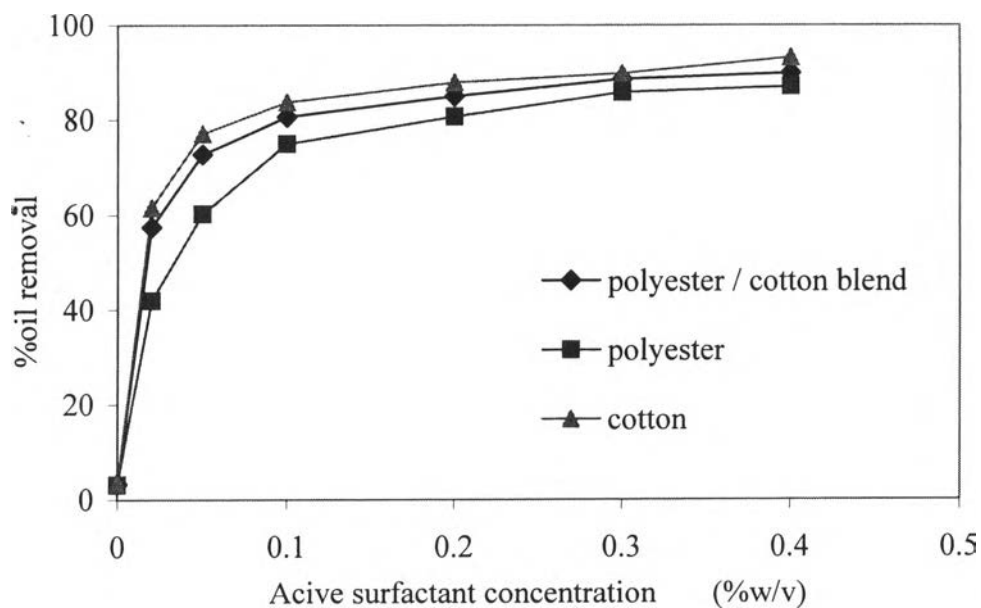


Figure 4.10 The effect of active surfactant concentration on oil removal on three types of fabrics at the optimum salinity (2.83 wt%) with the selected formulation.

4.5.2 Effect of NaCl Concentration on Detergency Performance

The effect of NaCl concentration on detergency performance was carried out by varying NaCl concentration at 0.115 % active surfactant of the selected formulation; 1.5wt% Dowfax 8390, 5wt% AOT and 5wt% Span 80. As the studied system contained a significant content of Dowfax 8390 and AOT (anionic surfactant), different salinity can induce different microemulsion types. The detergency performance of the studied system at different salinities is shown in Figures 4.11 and 4.12. With increasing salinity of the system, significant improvement of the detergency performance was obtained especially at very low salinity. The higher the NaCl concentration, the lower the repulsive force between head groups of anionic surfactant is obtained. Consequently, the tail group or hydrophobic part of surfactants can more adsorb more on highly hydrophobic oil droplets and fabrics. Hence, the oil removal of motor oil increases with increasing salinity.

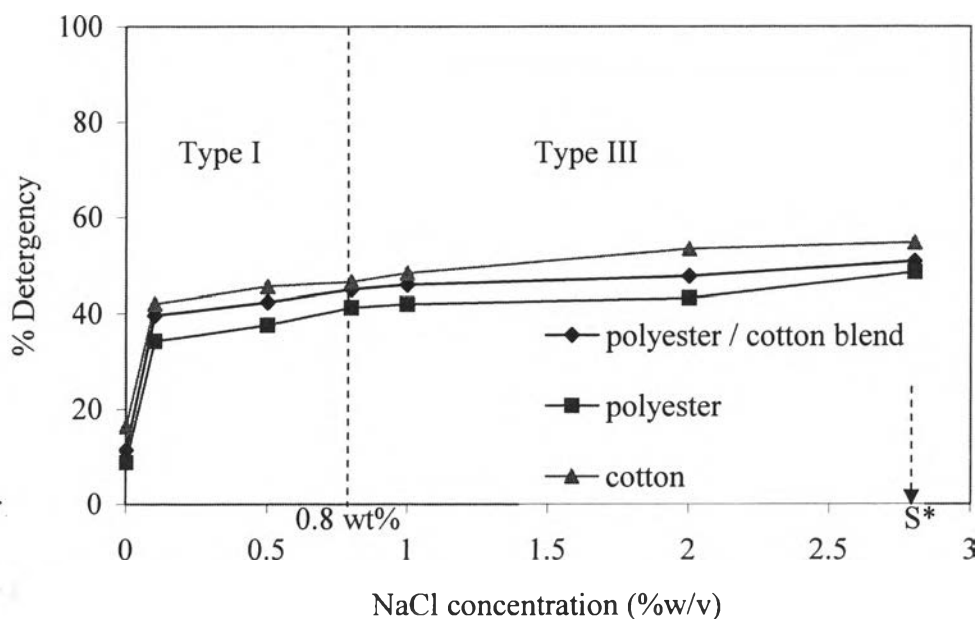


Figure 4.11 The relationship of %NaCl concentration and %detergency on three types of fabrics with the selected formulation at 0.115 active surfactant concentration.

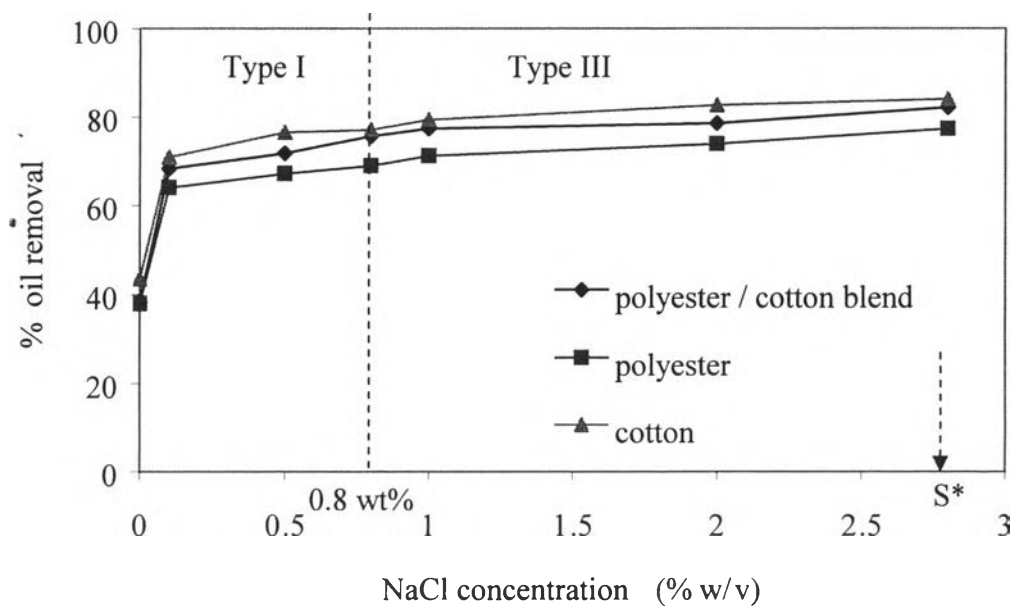


Figure 4.12 The relationship of NaCl concentration and oil removal on three types of fabrics with the selected formulation at 0.115 active surfactant concentration.

4.5.3 Correlation of Microemulsion Formation and Detergency Performance

Oil removal and IFT between the washing solution and the oil as a function of salinity are illustrated in Figure 4.13. The 0.115 active surfactant concentration is used in the washing process and the polyester/cotton blend was used as the substrate. To relate the phase study with the washing results, the system at 2.83 %NaCl was referred as the optimum condition of middle phase regarding to the lowest IFT value. As seen in Figure 4.13, the oil removal increases as the salinity increases. As expected the Winsor Type III region of microemulsion shows the highest oil removal at the optimum salinity that expresses the lowest IFT.

This detergency result shows the microemulsion formation of Winsor Type III microemulsion can improve detergency performance which is consistent with several studies.

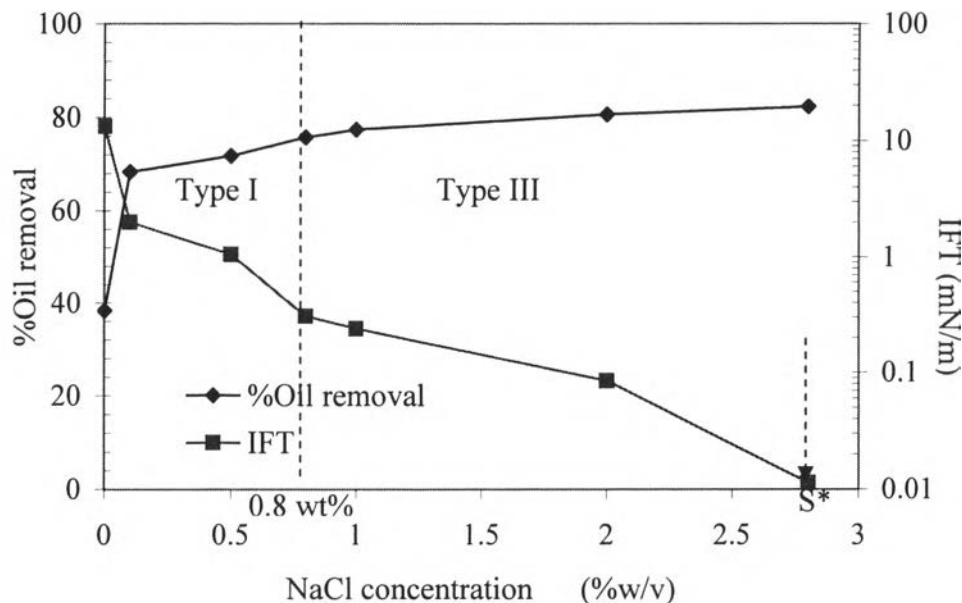


Figure 4.13 Oil removal and IFT between the washing solution and the oil as a function of salinity with two rinse steps using the studied formulation with 0.115 active surfactant concentration.

4.5.4 Effect of Amount of Rinsing Water and Number of Rinsing Step on Oil Removal

In this study, the washing experiment was done with the selected formulation (1.5% Dowfax, 5% AOT and 5% Span80) and 0.115% active surfactant at the optimum salinity. After the wash step was completed, three different rinse methods of 2, 4 and 6 rinses were compared with a same total rinsing water of 2000 ml. Therefore, 1000, 500 and 333.33 ml of distilled water were used for each of 2, 4 and 6 rinses, respectively.

The comparison of oil removal of each step in detergency process with different rinse methods is illustrated in Figure 4.14. By comparing the oil removal in each rinse, the oil removals of the wash step and the first rinse were quite high. Interestingly, for any rinse method, there was a significant difference in the oil removal between the first and the second rinse. These results show clearly that the amount of rinsing water affect the detergency performance in the first and the second rinse steps.

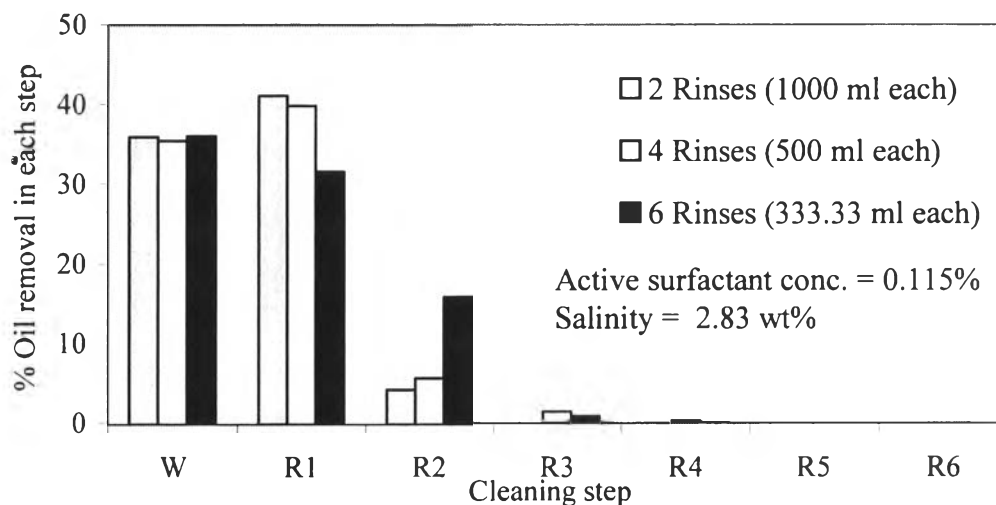


Figure 4.14 The oil removal of wash step and each rinse of rinse step using the selected formulation.

For all three rinse methods used, the result shows that very low the oil removal was almost none after the second rinse. Therefore, twice rinses are sufficient for detergency process. The explanation for this result is that the oil droplets might be penetrated in the fiber bundles and it is hard to detach the oil from the fabric. A better reason to explain this result relates to a lower amount of surfactants available in the third, fourth, fifth and sixth rinses that can be confirmed by the measured IFT values and it will be further discussed later.

The total oil removals of the washing and the rinsing steps with 2 rinses, 4 rinses, 6 rinses are illustrated in Figure 4.15. From this result, oil removal of the wash step (W) was very low in the range approximately 35-40 %. The detergency performance of the wash step (W) was insignificant different among three different rinse method since they were operated at the same conditions.

For the first rinse (R1) with different amounts of rinsing water, it shows the difference in the total oil removal, the total oil removal with 1000 ml rinsing water was very close to that with 500 ml rinsing water but the total oil removal with 333.33 ml decreased significantly. The result indicates that for a single rinse, there is a minimum amount of rinsing water required to maintain a desirable detergency performance.

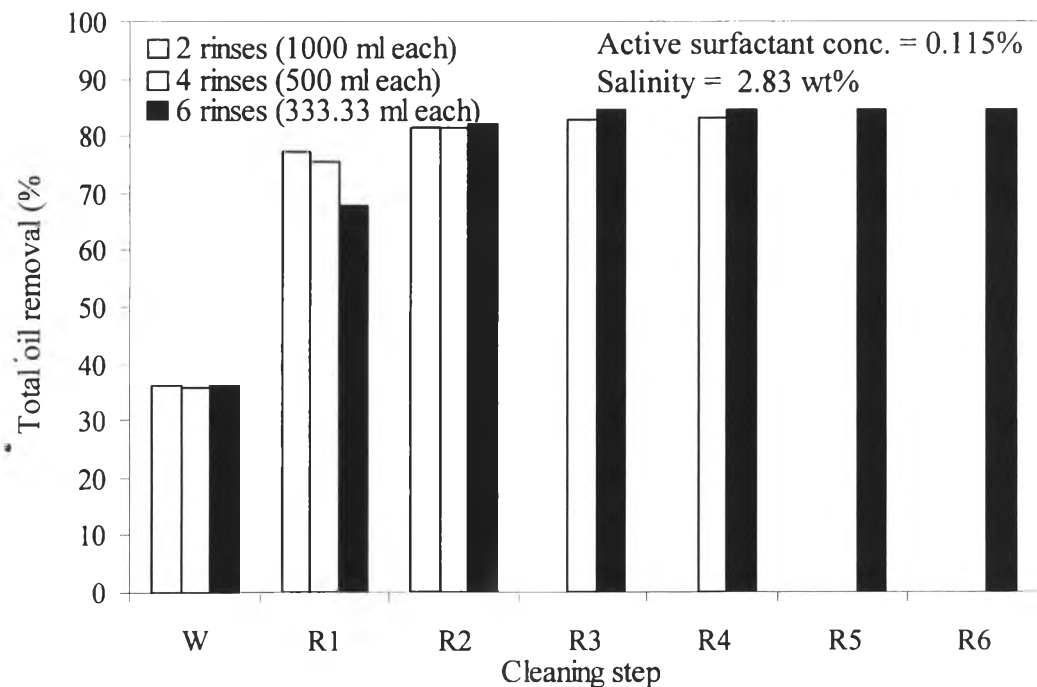


Figure 4.15 The total oil removal of each step with different rinse methods using the selected formulation.

According to the real application of the washing process, it is necessary to use a minimum quantity of rinsing water. Interestingly, it was found that the different amounts of rinsing water does not affect so much on the total oil removal provided that there are at least two rinses in operation as shown in Figure 4.15. The total oil removal is around 80%. From this result, the amount of rinsing water affects the oil removal of each step but does not affect the overall oil removal, therefore the low rinsing water can be used in real application.

4.5.5 Dynamic IFT during Rinse Step

The profiles of dynamic IFT between the rinsing water and dyed oil at different rinses are shown in Figure 4.16. For all three different rinsing methods, there was a spontaneous reduction of the dynamic IFT with the first rinse step. It indicates that the first rinse can remove oil quite highly because of the low IFT value. The reduction of IFT with time shows the oil is removed by the emulsification mechanism. In comparing the different quantity of rinsing water, an amount of water

1000 ml rinsing water showed the shortest time to form emulsion indicating that the system has the shortest time to removal oil from fabric. As shown in Figure 4.15, the highest oil removal of R1 is the 1000 ml rinsing water.

For considering the second rinse, only the 333.33 ml rinsing water showed the reduction of dynamic IFT and it showed the shortest time to form emulsion while both 1000 ml and 500 ml of rinsing water showed insignificantly lowering IFT. Therefore, for the second rinse, the highest oil removal was found at the 333.33 ml rinsing water.

In case of above the second rinse step, it shows the insignificant reduction of the dynamic IFT. As a result of high IFT in the system, there was almost none removal of oil above the second rinse.

4.5.6 Determination of Detergency Mechanism

The mechanisms of oily soil removal from fabric in the detergency process involves many factors such as interfacial energy, contact angle between oil and fabric, spreading and wetting. In this study, the dynamic and equilibrium interfacial tensions during the washing process were measured in order to gain a better understanding about the mechanisms in detergency process. Figure 4.17 shows the relationship between the oil removal and equilibrium IFT of each cleaning step at different rinses. The washing experiment was carried out with the selected formulation of 0.115 active surfactant concentration and at the optimum salinity of 2.83 wt%. From Figure 4.17, the wash step shows a very low IFT (0.001-0.01 mN/m) and has a reasonably moderate oil removal. The oil removal in this step is believed to be occurred by emulsification-solubilization mechanism relating to an increase in contact angle between the oil and the fabric surface as well as spreading of the oil on the fabric. By the presence of surfactant with a relatively large amount in washing step, the IFT value are very low or ultralow leading to spreading of oil droplet on fabric. As a result, it is more difficult for the oil to be removed completely. This is why the oil removal of the washing step in this study was not so high as expected due to its ultra low IFT. This find is a good agreement with previous results (Tongcumpua, 2003).

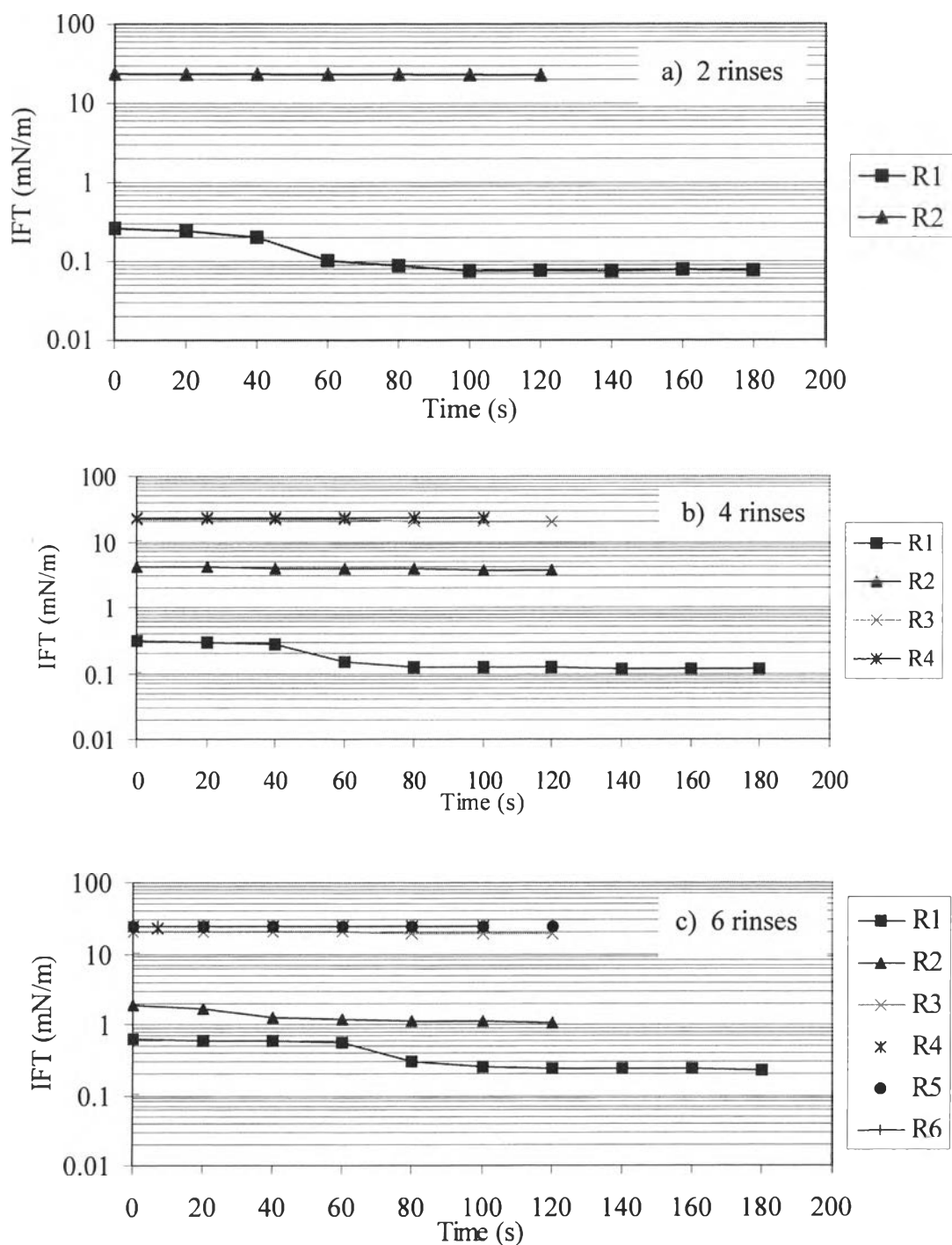


Figure 4.16 Profile of dynamic IFT between rinsing water and dyed oil at different rinses using the selected formulation of 0.115 % and at the optimum salinity of 2.83 wt%.

In the first rinse, the IFT was found to be much higher than that of the wash step, the spreading effect is reduced. As a result, the attached oil gradually form droplets and then detaches from the fabric. In addition, for all three rinsing method, it showed a relatively high oil removal in the first rinse. This result reveals that the detergency efficiency for oily soil removal increase with decreasing IFT of the system. However, the ultralow IFT can cause the spreading effect resulting in a significant reduction of oil removal. The work of adhesion (W_a) and the work of cohesion (W_c) are considered in order to provide an insight of the detergency process for oily soil removal. These parameters are expressed as follows (Thompson, 1994) :

$$\text{where } W_a = \gamma_{ow} (1 + \cos\theta) \quad (4.2)$$

$$W_c = 2 \gamma_{ow} \quad (4.3)$$

$$W_a - W_c = S \quad (4.4)$$

where W_a represents the work of adhesion, W_c represents the work of cohesion, γ_{ow} represents the interfacial tension between oil and washing solution and S represents the spreading coefficient. Therefore, if $W_a > W_c$, the spreading coefficient is positive, $\theta = 0^\circ$, and the oil spreads spontaneously over the substrate to form a thin film. If $W_a < W_c$, the spreading coefficient is negative, θ is greater than zero, and the oil does not spread over the substrate but the attached oil forms droplets or lenses with the finite contact angle and the oil droplets will be further removed by emulsification mechanism (Rosen, 1988). In case of the first rinse step, it shows a higher IFT than that in the wash step, the oil spreading effect is reduced. It can be expected that the contact angle in first rinsing step is not zero. Therefore, the value in the blanket of Equation (4.2) is not higher than 2. It means $W_c > W_a$, the oil droplets will detach from the fabric by emulsification mechanism. The IFT in the first rinsing step is low enough to occur the emulsification. In the second rinse, it showed a very high IFT for either 2 rinses or 4 rinses and the oil removal is relatively low as compared to that of the first rinse.

To maximize the detergency process for oily soil removal, an approach to obtain ultralow IFT by forming a Winsor Type III microemulsion should be considered. A proper design of the rinse step with a minimum quantity of rinsing water and two rinses is needed since the oil removal in the rinse step is as important as that in the wash step.

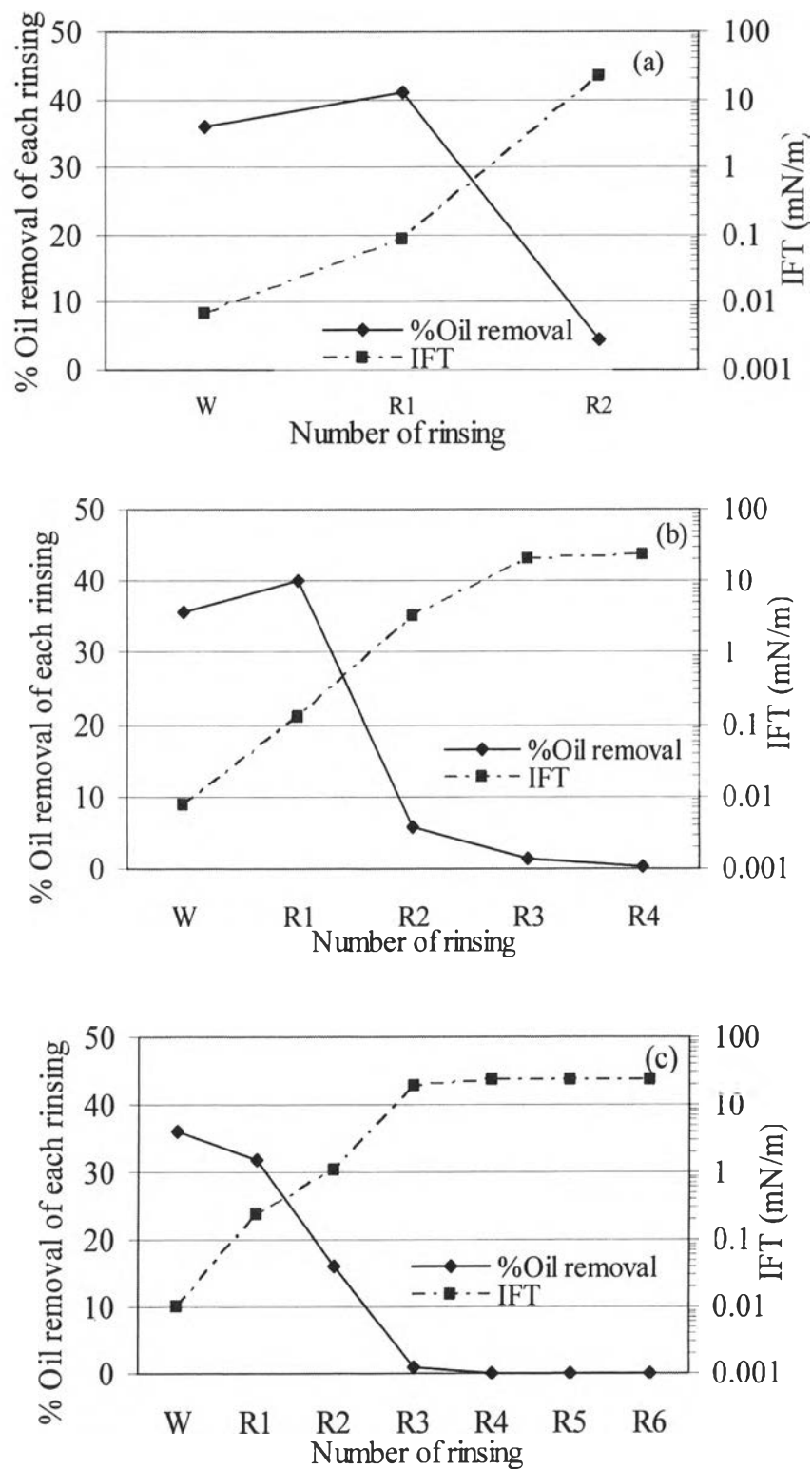


Figure 4.17 Correlation between equilibrium IFT and oil removal of each cleaning step with different rinses using the selected formulation of 0.115 active surfactant concentration and at the optimum salinity of 2.83 wt%.