CHAPTER V

MICROEMULSION FORMATION AND DETERGENCY OF OILY SOIL: V RESIDUAL SURFACTANT ON FABRIC

5.1 Abstract

Motor oil removal from a cotton/polyester blend fabric under conditions, at which a Winsor Type III microemulsion forms, was studied. Both ultralow oil/water interfacial tensions and high oil solubilization into the aqueous phase aid detergency in this region. A mixed surfactant system in a weight ratio of alkyldiphenyloxide disulfonate (ADPODS): sodium dioctyl sulfosuccinate (AOT): sorbitan monooleate (Span 80) of 1:10:6 was found to exhibit a Winsor Type III microemulsion at a very low salinity (2% NaCl). Both of oil removal and surfactant remaining in the rinse step at the optimum salinity were found to be much higher than those in the wash step because the residual surfactant on fabric during the wash step would come off with the oil droplet during the rinse step. Increasing the amount of rinse water beyond a low plateau level did not significantly affect the oil detergency. The higher the quantity of rinsing water, the lower the residual surfactant on the fabric surface.

Key words: Detergency, microemulsion, motor oil, residual surfactant, rinsing water

5.2 Introduction

Detergency can be defined as the removal process of unwanted materials from a fabric. Most detergency applications occur in an aqueous solution, although in dry cleaning, organic solvents are used instead. The discussion on the detergency of oily soil removal here is restricted to water-based systems [1]. The detergency process of oily soil removal is well accepted to consist of three mechanisms. Roll-up of oily soil is the primary mechanism, which is facilitated by increasing the contact angle exhibited by an oil droplet on the fabric surface in the presence of a bath (surfactant-containing solution). Emulsification, or snap-off, is the second mechanism, in which the oil droplets are partially drawn off into the washing liquid by hydrodynamic forces. The third is solubilization, in which detached oil molecules diffuse into the hydrophobic cores of micelles [1-3]. Regarding the roll-up mechanism, surfactant adsorption plays an important role in the detachment of oily soil. The adsorption of surfactants on the attached oil droplets on the fabric surface results in increasing contact angle which makes the oily soil detachment from fabric surface [1]. As a result, the surfactant adsorption during washing process can influence the oily soil removal efficiency since the solubilization and emulsification steps are affected directly by the concentration of micelle in the liquid phase.

A number of studies on the evolution of guidelines for superior oily soil removal have been investigated and reported since 1980s, and the most interesting approach, in recent literature, is a microemulsion-based formulation [2, 4-15]. Microemulsions exist in well-defined phase regions of multicomponent systems consisting of water, oil, surfactant, and electrolyte. The important characteristics of microemulsions are the ultralow interfacial tension (IFT), spontaneous formation, and high solubilization power towards both hydrophilic and lipophilic substances. Because of these extraordinary properties, microemulsions are of interest in textile detergency applications. A maximum oil removal has been found to correlate well with the minimum IFT of the system. In addition, a relationship between the IFT in the supersolubilization region, the oil-swollen aqueous micellar region close to the three-phase region, and a very high efficiency of oily soil detergency has also been reported [9-11]. Although, in the supersolubilization region, the IFT is not at its minimum and the solubilization parameter is not at its maximum at that point, the oily soil removal is quite close to the maximum value at the optimum salinity, and the complications of the presence of the three-phase system can be avoided.

To form microemulsions, the hydrophilic-lipophilic linker concept is considered to be an effective approach [16-20]. The use of a lipophilic linker is able to significantly enhance oil solubilization in the microemulsion phase without participating in the interfacial interactions. Unlike a co-surfactant which adsorbs at the interface, a lipophilic linker seems to be located inside the oil phase. The presence of a lipophilic linker would favor ordering of the oil molecules in one or several layers next to the interface, thus increasing the indirect interactions between the surfactant and the bulk oil [21]. It has been proposed that a surfactant system with a moderate hydrophilic/lipophilic balance (HLB) value, by using appropriate concentrations of the hydrophilic and lipophilic linkers, can give the best microemulsion performance [18-20, 22]. In our previous work, a formulation based on the linker concept was employed to form microemulsions with motor oil using mixed surfactants; sodium dioctyl sulfosuccinate (AOT), alkyldiphenyloxide disulfonate (ADPODS), and sorbitan monooleate (Span 80) [9-11]. In this work, a very high salinity (16%) was needed for this formulation to maximize a detergency performance, which is not practical for real applications in detergency.

For the latest detergency study with motor oil [15], a mixed surfactant system of 13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80 or 3:10:10 ratio of ADPODS:AOT:Span 80, which exhibited a Winsor Type III microemulsion at the optimum salinity of 2.83%, was formulated in order to avoid environmental problems from the use of high salinity (16%) in the previous formulation [9,10]. With this selected formulation, the effect of rinse cycle design was studied and it was observed that the use of two rinses was sufficient to obtain a high oil removal.

Interestingly, the spreading the attached oil droplets on fabric surface was found in the wash step for our previous works which are microemulsion-based formulations with ultralow IFT [10-11,15]. Subsequently, the oil could be only partially removed during the wash step and the remaining oil was further removed in the rinse step as high as that in the wash step. Therefore, the mechanism of oil removal in the wash step should include the spreading effect if a microemulsion-based formulation is used. In addition, it was hypothesized that the thin film was formed on the fabric surface in the wash step by partitioning of the surfactant from the washing solution onto the attached oil, resulting in continuity of the oil adsorbing on the fabric surface as well as penetrating into the fabric matrix. Consequently, a significant amount of oil still remains after the wash step. Therefore, the residual surfactant on fabric and residual surfactant concentration after each step in washing process should be considered in detergency process.

In this study, the concentrations of surfactant in both the washing and rinsing baths were investigated in order to study the effect of surfactant partitioning onto either the soil or fabric on the washing performance. Moreover, to follow up our previous work on studying the effect of rinsing method, the concentration of surfactant in each step at different rinse cycle designs was measured in order to evaluate the proper amount of rinse water used to achieve acceptable residual surfactant left on the fabric/soil surface with a high oil removal.

5.3 Experimental Procedures

5.3.1 Materials

Alkyl diphenyl oxide disulfonate (ADPODS or Dowfax 8390), which is a commercial grade anionic surfactant, was supplied by Dow Chemical Co. (Midland, MI, USA). Dioctyl sodium sulfosuccinate (Aerosol-OT or AOT) with 98% purity, which is a hydrophobic anionic surfactant with a negatively charged sulfosuccinate head group and an alkyl chain length of twenty carbon units, was obtained from Fluka Co. Sorbitan monooleate (Span 80), a nonionic surfactant, was obtained from ICI Uniquema Co, (Wilmington, DE, USA). Analytical grade NaCl was purchased from LabScan Asia Co, Ltd. Motor oil, which is commercially available for use in gasoline engines, type SAE 10W-30 (Castrol GTX), was used as a model oily soil. Oil red O (solvent Red 27, CI. No. 26125) was purchased from Aldrich Chemical Company, Inc. All chemicals were used as received without further purification. Standard unsoiled polyester/cotton blend (65/35) was purchased from Test Fabrics Co. (Middlesex, NJ, USA). Distilled water was used to prepare all surfactant solutions.

5.3.2 Phase Studies

Phase studies of microemulsions were conducted by salinity scan at 1:1 volumetric ratio of water to oil and 30 °C. The details of the procedure were described in our previous works [10-11,15]. After all studied microemulsion systems were incubated for 4 weeks to ensure equilibration, the height of each phase of microemulsions which was measured by using a cathetometer, (Titan Tool Supply, TC-II) attached to a digimatic height gauge (Mitutoyo, 192-631) with a high precision of ± 0.01 mm was used to determine their solubilization parameters of both oil and water. The solubilization parameter of oil or water means the volume (mL) of oil or water solubilized per unit weight (g) of surfactant [3]. The IFT values between the equilibrated phases were measured by using a spinning drop tensiometer (Krüss, SITE 04).

5.3.3 Surface Tension Measurement

The surface tension of surfactant solutions having different concentrations with and without NaCl was determined by the DuNouy ring technique using a tensiometer (Krüss, K10T). The surface tension measurement was conducted at 30 °C. The plot between surface tension vs total surfactant concentration was used to determine the critical micelle concentration (CMC).

5.3.4 Fish Diagram Study

In this work, the types of microemulsions were simply identified by the visual observation for total surfactant concentrations greater than 0.3%. At a total surfactant concentration lower than 0.3%, a condition, which was often not clearly visually observed, conductivity and IFT measurements were used to localize the types of microemulsions. The measurement of electrolytic conductivity is one approach that can be used to determine the microemulsion type [23,24]. For each condition, the electrolytic conductivity was measured, under gentle stirring with a magnetic stirrer, by using a conductivity meter (Cyberscan, con110). Since the aqueous phase contains a certain concentration of sodium chloride, the inversion is easily monitored by a change of two or more orders of magnitude in conductivity (ms/cm or µs/cm) [25]. The conductivity and the IFT results were used to plot the phase diagram or the conditions where Winsor Type I, II, and III microemulsions exist. When plotted as surfactant concentration vs salinity (or vice versa), these phase plots are called fish diagrams.

5.3.5 Fabric Preparation and Soiling Method

The testing fabric was pre-washed before soiling to eliminate the residues of mill finishing agents, which might interfere with oil removal performance. The prewashing step followed the ASTM standard guide D4265-98 [26]. The tested motor oil was dyed by the oil soluble Oil-Red-O dye using the standard method [27] before being applied to the testing fabric. Approximately 0.1 g of the oil-soluble dye was added to 100 mL of the oil. The colored oil was filtered until clear. The soiling procedure was done by diluting 10 mL of the clear dyed oil with dichloromethane to 100 mL. An 18×8 inch fabric sample was folded and placed in a glass container, and then the dyed oil solution was poured into it until the fabric was completely submerged. It was left for 1 min before being rinsed to remove the adhered solution. The soiled fabric was then unfolded and laid on a flat plate in a ventilated hood to dry at room temperature overnight in order to dry the soiled fabric. After that, the soiled fabric was cut into 3×4 inch swatches in wrap and weft directions. All swatches were freshly prepared for each batch of the laundry experiment. By this soiling method, the average weight ratio of oil to fabric was approximately 0.19.

5.3.6 Laundry Procedure

Detergency experiments were carried out by using a tergotometer (Copley, DIS 8000). The tergotometer simulates home washing-machine action in a bench scale unit. The washing experiments were performed in a 1000 mL washing solution with 20 min washing time. To investigate the effect of rinsing more thoroughly, the total volume of rinsing water used was kept constant at 2000 mL, while the volume of rinsing water for each rinse step was varied for three sets of experiments at 1000, 500, and 333.33 mL, which corresponded to 2, 4, and 6 rinses, respectively. The first rinse took 3 min, while each subsequent rinse step took 2 min. All experiments were carried out at a constant temperature of 30 °C. Three soiled swatches were washed together for one cycle as replications. In order to determine the correlation between phase behavior and detergency performance, NaCl was added to the washing solutions to obtain the same salinity as that in the Winsor type III microemulsion region in the phase studies. In addition, a commercial grade detergent (Unilever, Breeze Excel), available in the Thailand marketplace, was also used at the same total concentration without salt in order to compare the detergency performance with the selected formulation.

5.3.7 Oil Removal Measurement

Oil removal is characterized by portion of residual oil on the swatches which is washed out during the detergency process. The attached oil was extracted from the fabric sample by submerging a swatch in 2-propanol overnight at room temperature and the amount of extracted oil in the solution was measured by absorbance using a UV/VIS Spectrophotometer (Shimadzu, 2550), a procedure discussed by Goel [28].

5.3.8 Dynamic IFT Measurement

Dynamic IFT measurements were carried out using a spinning drop tensiometer (Krüss, SITE 04) at 30 °C. The heavy phase was the aqueous washing solution or rinsing solution, and the light phase was the dyed oil. A volumetric ratio of the aqueous solution to the oil of 100:1 was used to measure IFT values. The diameters of the oil drop were measured as a function of time, while the rotational velocity was held constant.

5.3.9 Surfactant Concentration Measurement

The ADPODS concentration, in both washing and rinsing solutions, was measured by the UV/VIS spectrophotometer at a wavelength of 235 nm, which was shown to be the highest absorbance for ADPODS. The concentration of AOT and Span 80 were assumed to be in the same proportion as that of ADPODS. The surfactant residue on the fabric's surface of each step was calculated by the concentration difference method, assuming that the surfactant adsorption on the glass container in the detergency experiments was negligible.

5.4 Results and Discussion

5.4.1 Effect of Surfactant Composition on Microemulsion Formation

In this study, the mixture of ADPODS, AOT, and Span 80 was used to form microemulsions with motor oil at different concentrations of each surfactant in order to minimize the NaCl required. When the system was scanned with any concentration of ADPODS, AOT, or Span 80, the other two surfactant concentrations were kept constant. Each of the surfactant concentrations was varied to find a proper formulation that formed microemulsions at the lowest salinity. SP is defined as the volume of oil solubilized (SPo) or of water solubilized (SPw) per weight of total surfactants in the microemulsion phase. SP values were plotted as a function of salinity; the interception of SPw and SPo can be used to indicate the optimum salinity (S*) and the optimum solubilization parameter (SP^*). In previous work [15], it was observed that the NaCl concentration needed to form a Winsor Type III microemulsion decreased significantly with increasing AOT concentration. Therefore, studying the effect of AOT concentration was used as the starting point in this work.

In order to observe the effect of AOT concentration on the microemulsion formation with motor oil, both ADPODS and Span 80 concentrations were fixed at 1% and 3%, respectively, while the AOT concentration was varied from 3% to 5%. As shown in Figure 5.1a, the higher the AOT concentration, the lower the salinity is needed for middle phase microemulsion formation. This can be explained by the fact that an increase in AOT concentration simply decreases the HLB of the system, it thus compensates the salinity needed to form a Winsor Type III microemulsion. From the scan of AOT, the mixture system that showed the lowest optimum saliniy (2.6% NaCl) had the compositions of 1% ADPODS, 5% AOT, and 3% Span 80. This formulation was selected to subsequently study the effect of ADPODS concentration.

The AOT and Span 80 concentrations were fixed at 5% and 3%, respectively, while the ADPODS concentration was varied from 0.5% to 1%. The effects of ADPODS concentration on solubilization parameters are illustrated in Figure 5.1b. In contrast with AOT, ADPODS is a highly hydrophilic surfactant with an HLB value higher than 41 [28], an increase ADPODS concentration in the system results to increasing HLB of the system. Consequently, the higher the ADPODS concentration, the higher the salinity is neded for the phase transition from a Winsor Type I to Winsor Type III. Microemulsion.

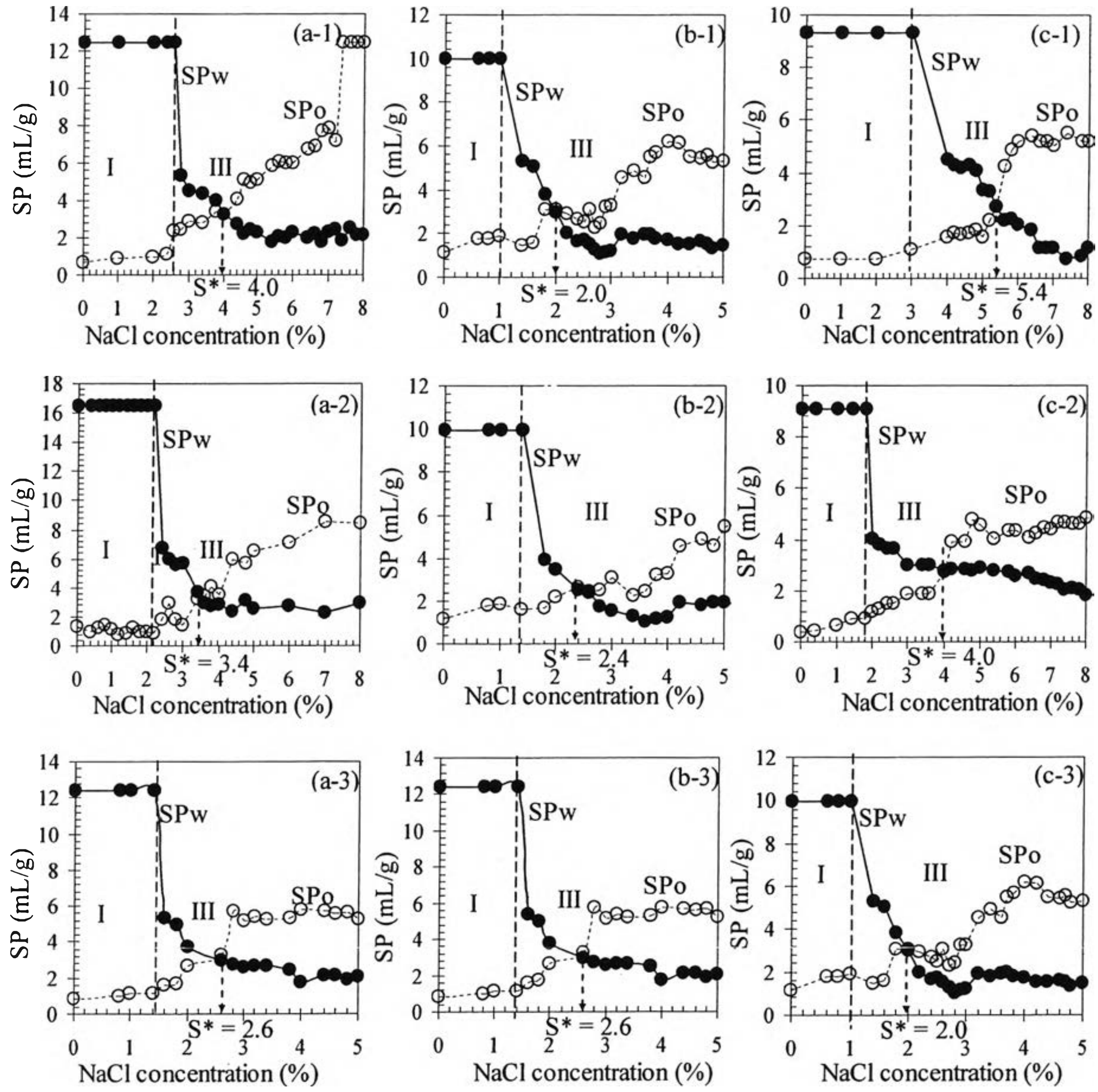

Figure 5.1 Solubilization parameters (SP) and Winsor Types of microemulsions as a function of salinity at an initial oil-to-water volumetric ratio of 1 to 1; (a) 1% ADPODS and 3% Span 80 were fixed, (a-1) 3% AOT, (a-2) 4% AOT and (a-3) 5% AOT; (b) 5% AOT and 3% Span 80 were fixed, (b-1) 0.5% ADPODS, (b-2) 0.75% ADPODS and (b-3) 1% ADPODS; (c) 0.5% ADPODS and 5% AOT were fixed, (c-1) 1% Span 80, (c-2) 2% Span 80 and (c-3) 3% Span80. SP* is SP at optimum salinity S* where SP of oil (SPo) equals SP of water (SPw) into middle phase microemulsion phase.

This can be obviously seen that the optimum salinities of the systems containing ADPODS at 0.5%, 0.75% and 1.0% are 2.0%, 2.4% and 2.6% NaCl, respectively (see Figure 5.1b-1 to b-3). To achieve the lowest optimum salinity for the purpose of this study, the system of 0.5% ADPODS, 5% AOT, and 3% Span 80 was selected for further investigation.

To observe the effect of Span 80 concentration of the mixed surfactant system on microemulsion formation, both the ADPODS and AOT concentrations were fixed at 0.5% and 5%, respectively, while the Span 80 concentration was varied from 1% to 3%. The result can be expected to obtain a lower optimum salinity with increasing Span 80 since Span 80 is the most lipophilic surfactant for this study (HLB = 4.3). In the same manner with the AOT scan, the result shows that the higher the Span 80 concentration, the lower the salinity is needed for middle phase microemulsion formation (Figure 5.1c-1 to c-3). However, since Span 80 is more lipophilic than AOT, one may observe that the change of 1% Span 80 affect more on the optimum salinity change. The system that shows the lowest optimum salinity (2% NaCl) from the scan of Span 80 was the mixture of 0.5% ADPODS, 5% AOT, and 3% Span 80, which is slightly lower than in our previous work (2.83% salinity) [15]. Therefore, this formulation was used to conduct the detergency experiments.

5.4.2 Effect of Surfactant System on Detergency Performance

The selected formulation consisting of 0.5% ADPODS, 5% AOT, and 3% Span 80 which is equivalent to a weight ratio of ADPODS:AOT:Span 80 of 1:10:6, was used for the detergency experiments. For detergency experiments, the selected formulation with an original concentration of 8.5% was diluted to obtain 0.119% laundering bath close to that used in the previous work (0.115%). Figure 5.2 shows the detergency results and the equilibrium IFT at various salinities of the selected formulation, compared to each single surfactant system and the commercial liquid detergent at the same total surfactant concentration of 0.119%. In comparisons among the three single surfactant systems, it was observed that the ADPODS system gave a much higher oil removal than both the AOT and Span 80 systems, especially at high salinity. Moreover, the oil removal of either the single ADPODS or AOT system was clearly higher than the commercial detergent. Interestingly, the oil removal of the ADPODS system increased with increasing salinity and it was much higher than that of the AOT system even the ADPODS system providing the higher IFT than the AOT system. As expected, the selected formulation of 1:10:6 ADPODS:AOT:Span 80 weight ratio gave the highest oil removal at any given salinity, compared with all the single surfactant systems, as well as the commercial detergent.

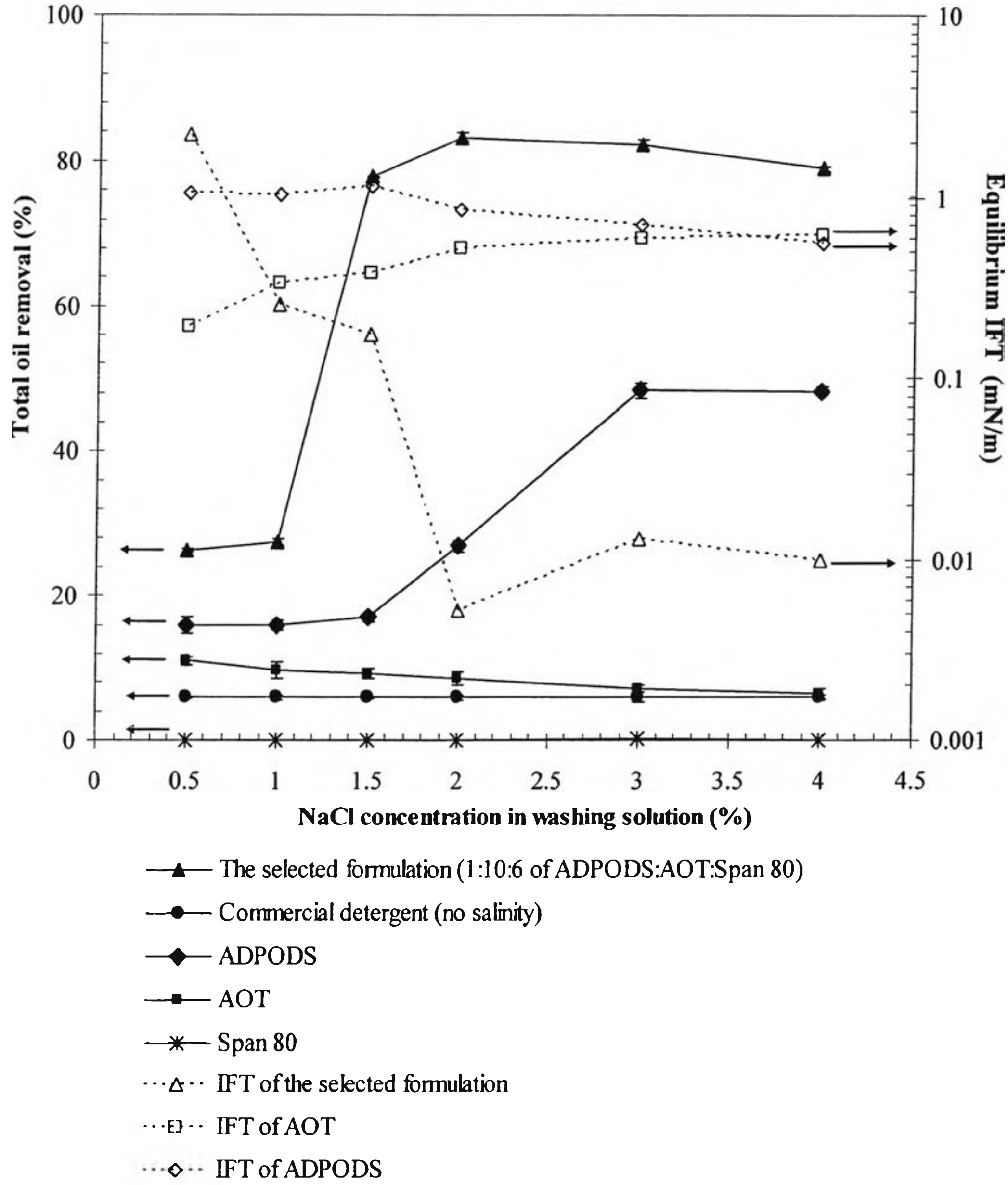

Figure 5.2 Effect of surfactant system (both single and mixed surfactant systems) on both total oil removal and IFT on a polyester/cotton blend (65/35) at various salinities and a total surfactant concentration of 0.119% compared to a commercial liquid detergent.

The explanation for this result is that the presence of both ADPODS and AOT, anionic surfactants, causes an increase in the contact angle of the attached oil droplets, promoting the detachment of the attached oil. For the case of the mixed surfactant system used here, the presence of Span 80 as a nonionic surfactant can only enhance the solubilization of the detached oil into micelles. However, the single Span 80 system cannot increase the contact angle of the attached oil on the fabric as high as any anionic surfactant, leading to very low oil removal performance. Again, it can be explained in that the selected formulation consisting of the three surfactants having very high, moderate, and very low values of HLB, can provide both a high increase in the contact angle and high solubilization capacities for both oil and water, leading to having a very low or ultralow IFT in the system, as also shown in this figure. In comparisons among studied surfactant system at the optimum condition (2% NaCl) the IFT of the selected formulation was extremely lower than those of the three single surfactant systems. Therefore, it again confirms that decreasing IFT and increasing solubilization play a very important role to promote the oil removal [29].

5.4.3 Fish Diagram of Motor Oil with the Selected Formulation

The fish diagram has been used to describe the phase behavior of microemulsion systems as a function of salt and surfactant concentrations for decades [30-35]. For an ionic surfactant system, the fish diagram looks like a lower case Greek gamma with a 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 very high surfactant concentrations and corresponds to the whole solution being a single homogeneous surfactant-rich phase [31]. If a studied system consists of oil, water, and nonionic surfactant, the role of salt or cosurfactant is replaced by temperature [33,34].

Since detergency is generally applied at a moderate surfactant concentration for cost reasons (0.119% for the present washing experiments), in the present work, the fish diagram was not investigated at very high surfactant concentrations. Hence, the Type III to IV transition was not able to be observed. In fact, the most important parameter from the fish diagram for this research is the critical microemulsion concentration (CμC), which is the minimum surfactant concentration needed to form a middle phase (Winsor Type III) microemulsion. Figure 5.3 illustrates the IFT of an equilibrium system and dynamic system as a function of total surfactant concentration of the selected formulation (1:10:6 of ADPODS:AOT:Span 80). The equilibrium system was obtained after 1 month while the dynamic system was taken at 20 min. Both parameters in terms of equilibrium and dynamic IFTs tended to decrease with increasing total surfactant concentration. Typically, there are two steps of the sharp decrease in IFT with increasing surfactant concentration. For a surfactant concentration lower than the CMC, IFT decreases with increasing surfactant concentration because of the surfactant adsorption at the oil-water interface, and the first sharp drop of IFT corresponds to the CMC at which a first micelle starts to form. The second sharp drop corresponds to the change in curvature of the micelles, which ends at the point where the first droplet of a Winsor Type III microemulsion forms; and this corresponding surfactant concentration is known as the CμC [36]. From this observation, the CMC and CμC were found at 0.007% and 0.07% of total surfactant concentration, respectively.

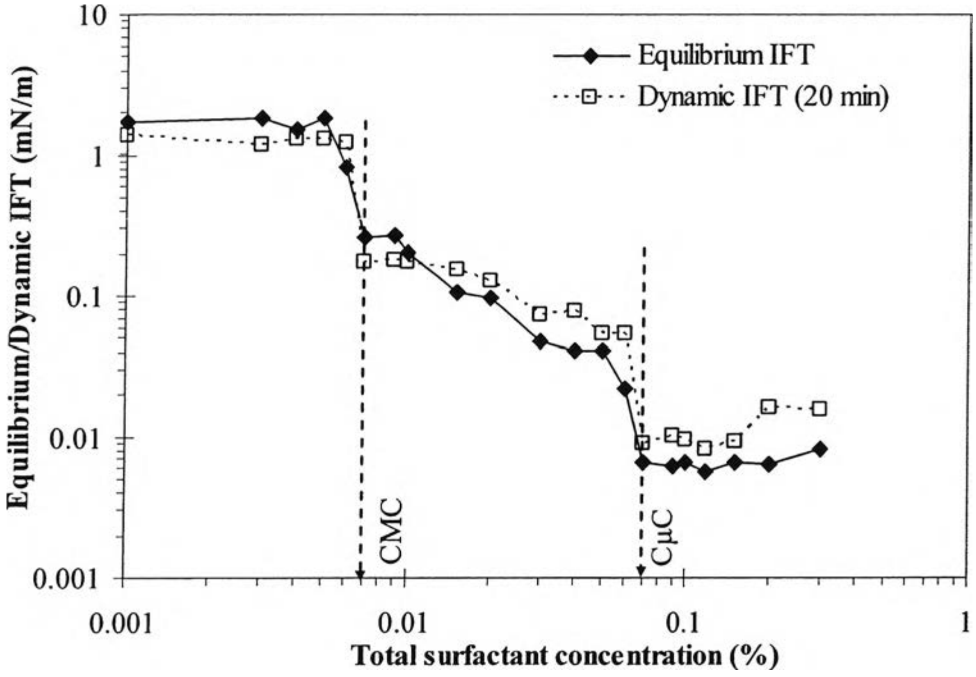

Figure 5.3 Equilibrium and dynamic IFT at 20 min as a function of total surfactant concentration at 30 °C using the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio).

The CMC value obtained from Figure 5.3 is also confirmed by the CMC value determined from the plot between surface tension and total surfactant concentration, as shown in Figure 5.4. For comparisons of the equilibrium IFT and the dynamic IFT, equilibration time does not affect both values of the CMC and the CμC. Then, it is reasonably acceptable to apply the CμC obtained from the fish diagram for the conditions used in our washing experiments, which were operated for 20 min of washing time.

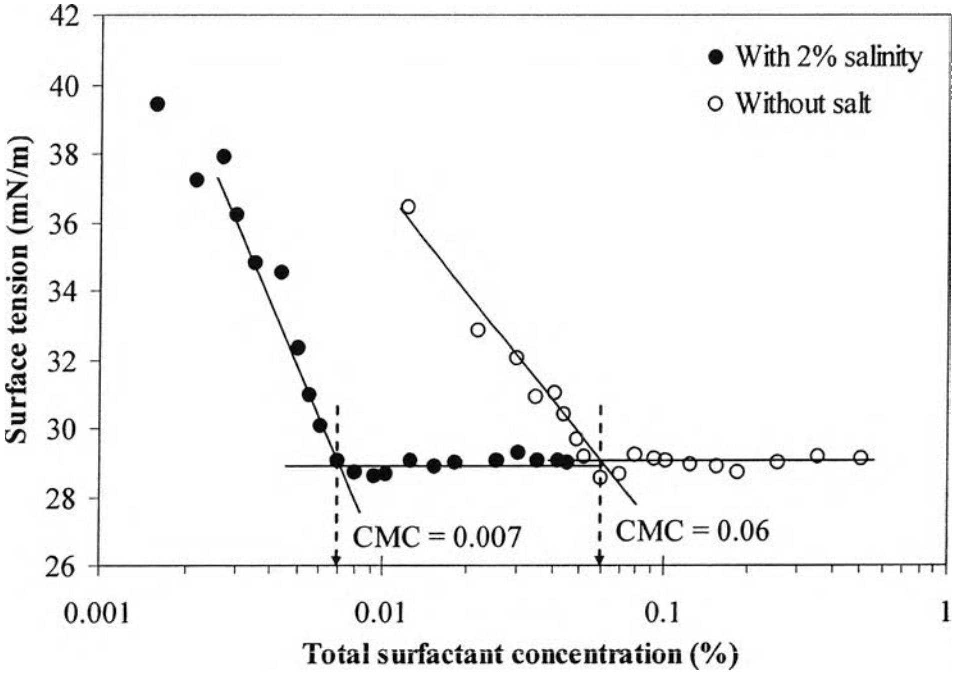

Figure 5.4 Surface tension plot with total surfactant concentration of the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio) with and without salinity.

Figure 5.5 illustrates the fish diagram of the selected formulation at 1:1 oil-to-surfactant volumetric solution ratio and 30 °C. The fish diagram was constructed by using the visual observation at high surfactant concentrations and using both the conductivity and IFT data at low surfactant concentrations. The CμC was found at a very low surfactant concentration of 0.07%. From the fish diagram, the selected formulation can provide a wide region of Winsor Type III microemulsions in the salinity range of 1 to 10%. Interestingly, the total surfactant concentration of 0.119% in the washing bath used for the detergency experiments is located in the Winsor Type III region, which is slightly higher than the CμC (0.07%) and much higher than the CMC (0.007%). Therefore, it can be noted that the diluted formulation used as the washing bath in the detergency experiments can still provide the middle phase microemulsion condition, which is necessary for high detergency performance.

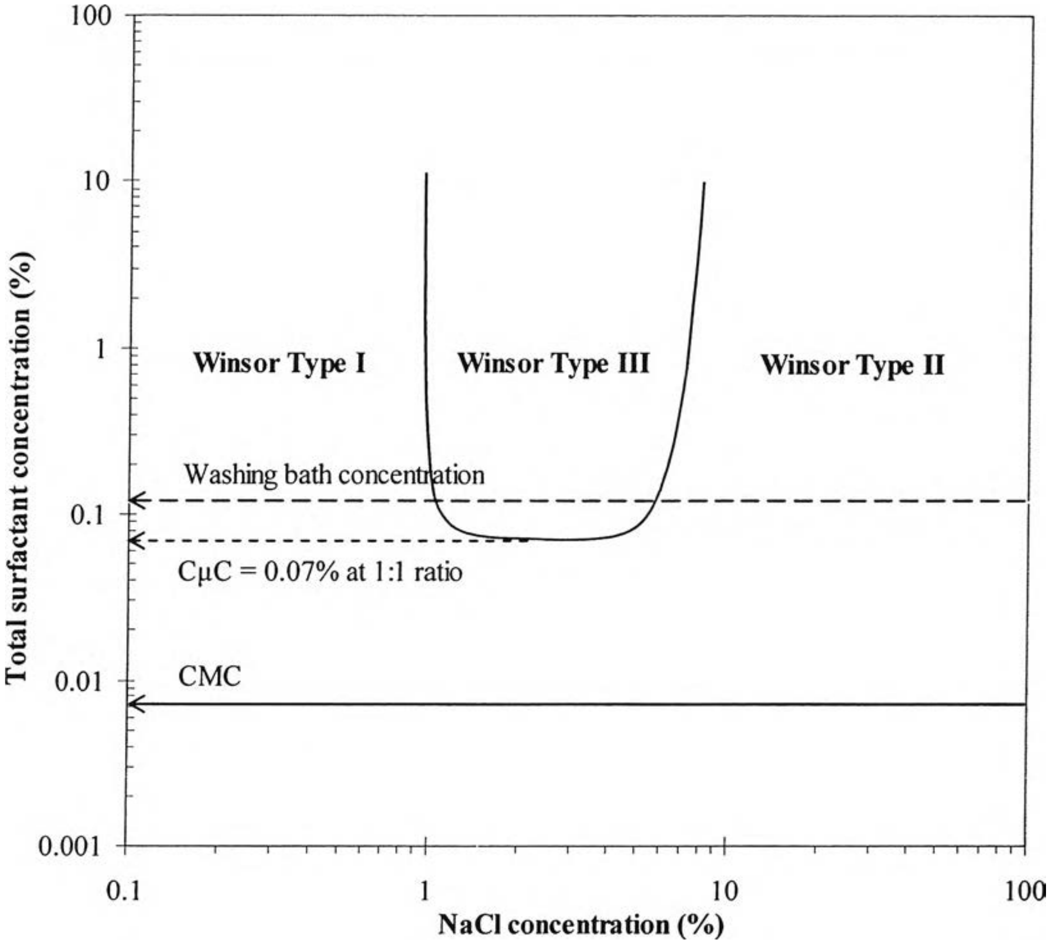

Figure 5.5 Fish phase diagram of the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio) at an oil-to-water volumetric ratio of 1 to 1 at 30 °C.

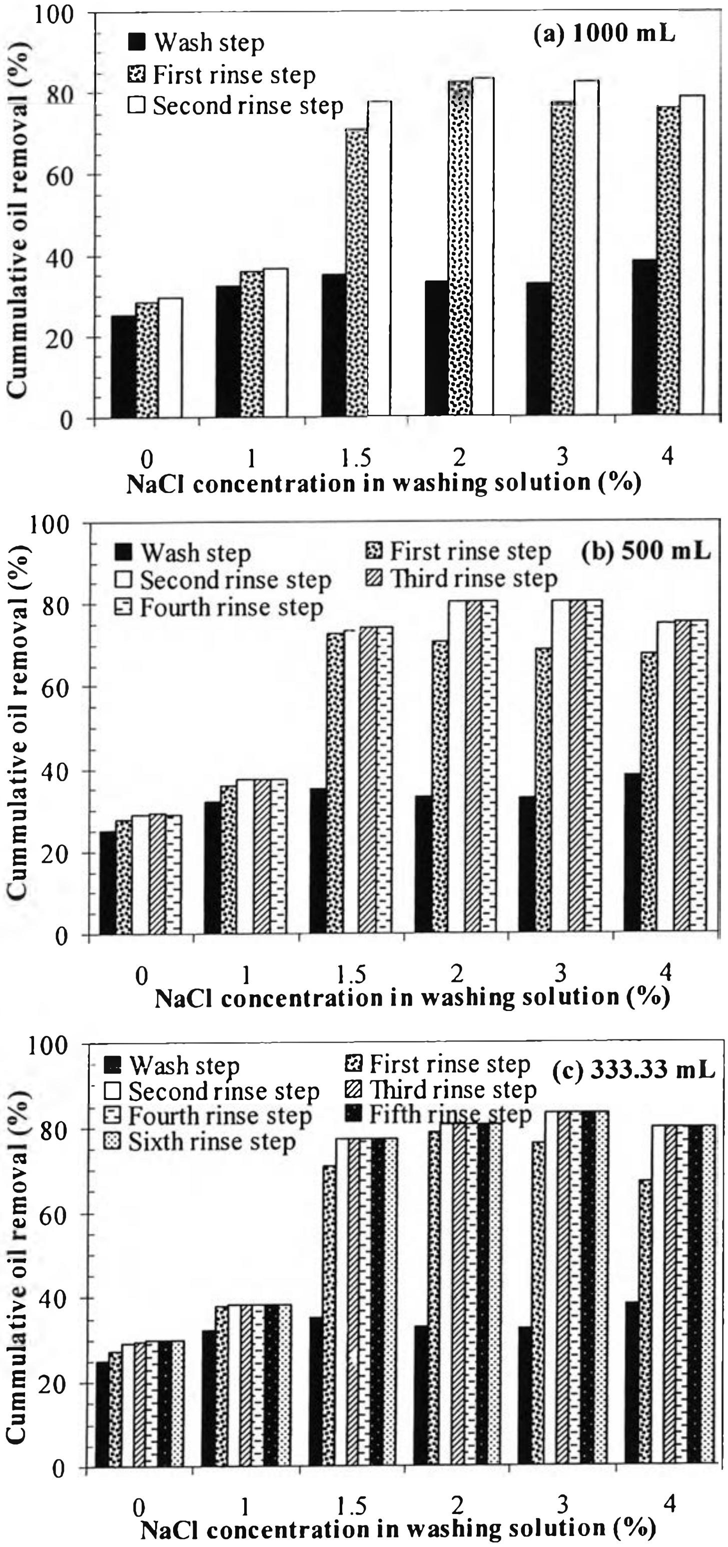

Figure 5.6 The cumulative oil removal of different rinsing methods (a) 1000 mL, (b) 500 mL, and (c) 333.33 mL for each rinse using the selected formulation of total surfactant concentration of 0.119% at different salinities.

5.4.4 Effect of Amount of Rinsing Water on Oil Removal

In this study, the washing tests were done with 1000 mL of the washing solution and 2000 mL of total rinsing water with different numbers of rinses (2, 4, and 6). The cumulative oil removal of each step with different amounts of rinsing water at different NaCl concentrations, and the total oil removal at different rinsing methods with various salinity are illustrated in Figures 5.6 and 5.7, respectively. For any given rinsing method, the oil removal in the wash step was considerably lower than that in the rinse step when the salinity of the washing solution was close to or higher than the optimum salinity (2%) and the insignificant increase in oil removal beyond the second rinse was found in the studied range of salinity. Interestingly, total oil removal was almost the same for different rinse cycle designs, suggesting that the oily soil detergency performance does not rely on the rinsing method under the studied conditions with the selected formulation. From this result, it can be concluded that the use of 333.33 mL of distilled water (one third of washing solution) with only two rinses is sufficient for the detergency process to obtain a reasonably high oil removal excluding the residual surfactant on the fabric surface after washing.

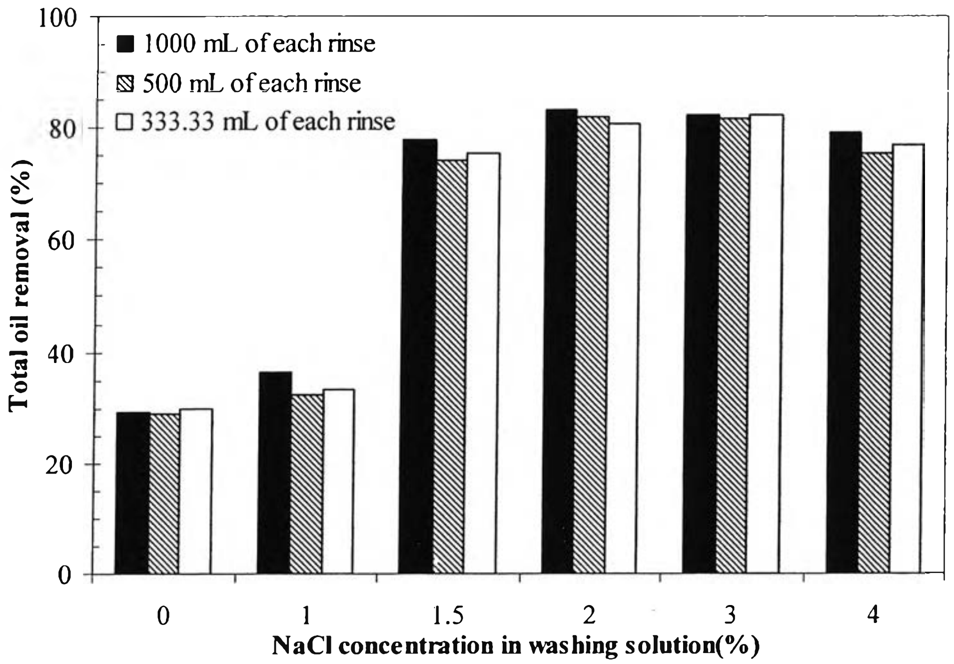

Figure 5.7 Total oil removal with different volumes of rinsing water and different salinities using the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio).

5.4.5 Correlation between IFT and the Total Oil Removal Using the Selected Formulation

The IFT between the washing solution having 0.119% total surfactant concentration and the dyed oil was measured in order to investigate the relationship of the IFT with the total oil removal of the whole washing process. As shown in Figure 5.8, the IFT value of the washing solution during the wash step is very low in the range of 0.008-2 mN/m. With increasing salinity of the washing solution below the optimum salinity (2%), the oil removal increased, whereas the IFT decreased. The oil removal reached a maximum value (≈ 80%) but the IFT reached a minimum at the optimum salinity. In contrast, beyond the optimum salinity, the IFT increased gradually with increasing NaCl concentration, whereas the oil removal slightly decreased. Interestingly, the IFT of the washing solution at the maximum oil removal was considered to be around 0.008 mN/m, which is in the ultralow range (10^{-1}-10^{-3} mN/m).

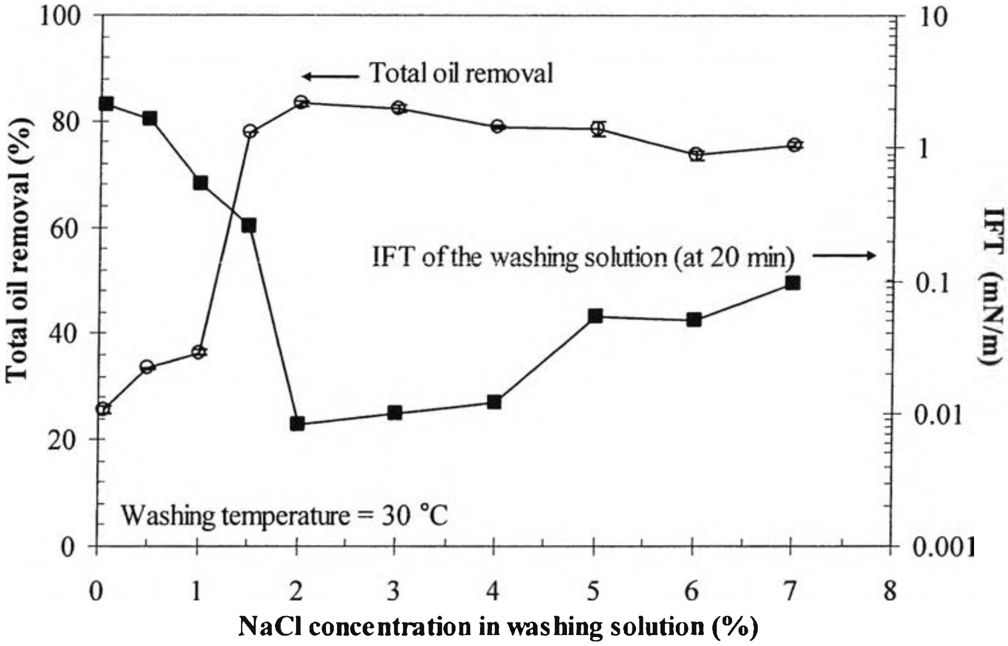

Figure 5.8 Total oil removal and IFT of the washing solution as a function of salinity with the 0.119% surfactant concentration of the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio) and two rinses of 1000 mL each.

Moreover, it is worth noting that at 1.5% salinity, which is in the supersolubilization region, the IFT of 0.26 mN/m was considerably low but not ultralow, but the oil removal was found to be as high as that at the optimum salinity. This result agrees well with our previous study [10,15]. Even though the IFT of the washing bath was correlated well with the detergency performance, there might still has another important factor affecting the detergency performance which is related to the presence of a testing fabric in luandering process. Hence, it is hypothesized that the surfactant left onto the surface of the testing fabric might play a significant role in the detergency performance, which will be discussed later in this paper.

5.4.6 Correlation between IFT of Washing Solution and Oil Removal in the Wash Step

In order to obtain a better understanding of the washing process, the oil removal in the wash step was investigated apart from the total oil removal. Figure 5.9 shows the relationship between the IFT and the oil removal in the wash step as a function of salinity. In addition, the amount of ADPODS remaining in the washing solution at the end of the wash step was also shown in this figure which will be discussed in detail latter. With increasing salinity, the IFT between the oil and washing solution sharply decreased and reached a minimum at the optimum salinity (2%). Beyond the optimum salinity, the IFT tended to increase slightly with increasing salinity. Interestingly, in the wash step, the oil removal was relatively low (31-32%) in the studied range of salinity. As reported before, the low oil removal in the wash step results from the spreading effect [11]. In a comparison between the total oil removal and the oil removal in the wash step, most oil was removed in the rinse step instead of the wash step, when the system salinity was close to or greater than the optimum. The present results are in good agreement with our previous study [10].

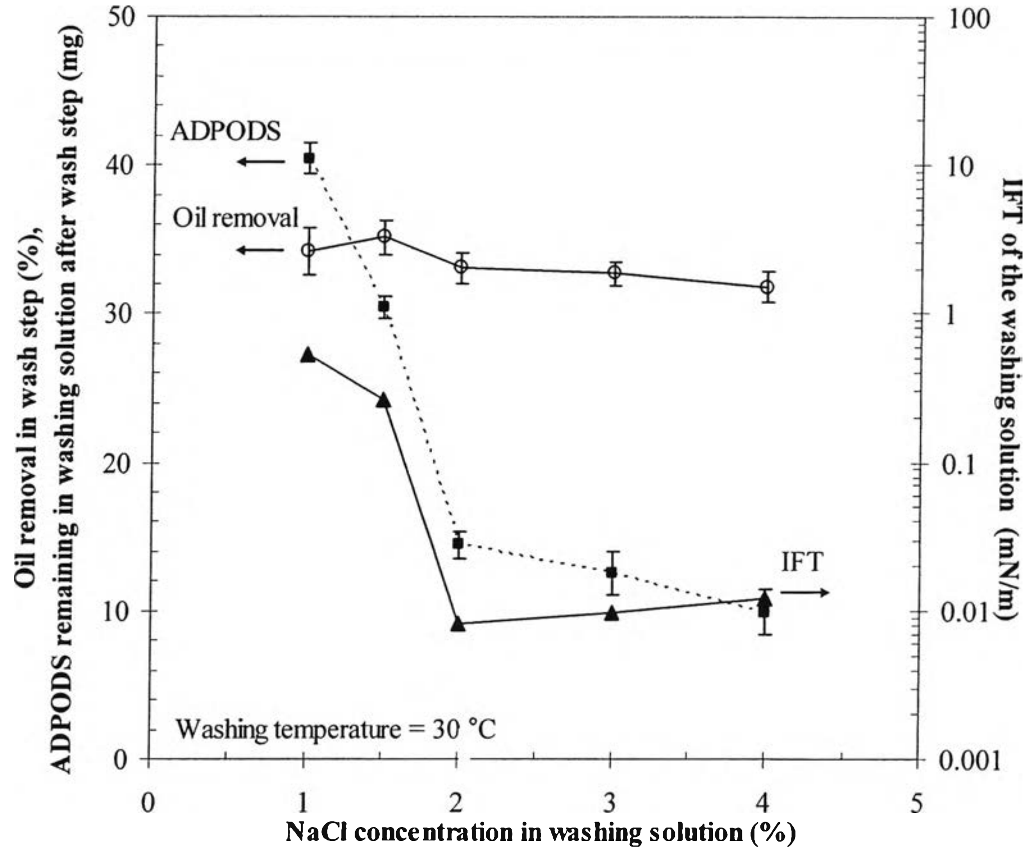

Figure 5.9 The relationship between the IFT and the remaining ADPODS in washing solution and the oil removal in the wash step as a function of salinity with the 0.119% surfactant concentration of the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio).

5.4.7 Correlation between Equilibrium IFT and Oil Removal in Washing Process

Figure 5.10 illustrates the oil removal in either the wash step or rinse step relating to the values of equilibrium IFT from the present study, as well as from our previous work. As can be seen in Figure 5.10, during the wash step, the oil removal decreases with decreasing IFT below 0.1 mN/m. The ultralow IFT in the wash step can result in the spreading effect to cause the oil droplets to spread over the fabric surface and penetrate into the fabric matrix, leading to low oil removal [11]. The maximum oil removal was found to be in the IFT range of 0.01 to 0.1 mN/m. For the IFT in the range of 0.1 to 3 mN/m, the oil removal decreased sharply with increasing IFT. This finding indicates that detergency performance is governed predominantly by the IFT of the system. Therefore, to obtain acceptably oil removal in detergency process, IFT should be lower than 1 mN/m. In general, a decrease in the system IFT may not improve oil removal, especially at ultralow range, it can even reduce oil removal. However, the benefit of ultralow IFT can give a better oil removal at the subsequential rinse step, resulting in the enhancement of total oil removal.

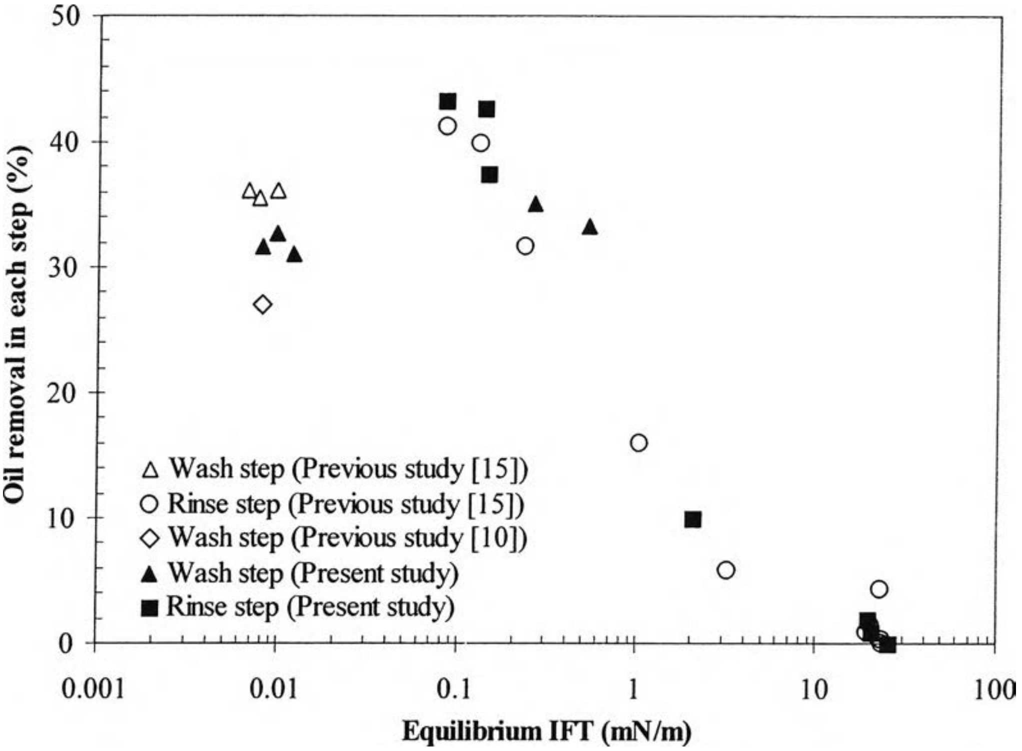

Figure 5.10 Oil removal in each step related to the equilibrium IFT between washing solution and oil at different salinities with the selected formulation (1:10:6 of ADPODS:AOT:Span 80).

5.4.8 Correlation between Remaining ADPODS in Washing Solution and Detergency Efficiency

In this study, only the ADPODS concentration in the washing solution was determined, due to the analytical instrument available. However, it is reasonable to assume that the concentrations of the other two surfactants could exhibit the same proportional trend as the concentration of ADPODS. Figure 5.9 shows the ADPODS amount remaining in the washing solution after the wash step as a function of salinity. The ADPODS amount in the washing solution tended to decrease with increasing salinity, suggesting that a higher amount of surfactant left on the fabric surface with increasing salinity. The increase in the surfactant adsorption onto the fabric surface and the attached oil at the higher NaCl concentrations results in decreasing IFT of the system. The increasing surfactant adsorption with increasing NaCl concentration is due to the reduction of the electrical double layer of the head portions of ADPODS and AOT by the sodium counterion (Na^+). From the results, at the optimum salinity (2%), 79.4% of the initial ADPODS amount of 70 mg was found to adsorb onto the fabric surface during the wash step, suggesting that the residual surfactants on fabric/soil plays a significant role in the detergency performance of oil removal in the subsequent rinse step. More explanation will be given in the last paragraph of this section.

To investigate the role of surfactant adsorption, the ADPODS concentrations in the rinsing solutions with different rinsing methods were measured. The ADPODS amounts present in the rinsing solutions after the first and second rinses using different rinsing methods are shown in Figure 5.11. The ADPODS amount was calculated only in the first and second rinsing solutions because the ADPODS concentrations beyond the second rinse were very low. For any given rinsing method, the ADPODS amount in the first rinsing solution was quite high as compared to that in the second rinsing solution. For the first rinse with any given rinsing water volume, the ADPODS amount tended to increase with increasing salinity and the highest ADPODS amount was found at around the optimum salinity. Beyond the optimum salinity, the ADPODS amount tended to decrease slightly with increasing salinity. In addition, it was observed that the higher the amount of rinsing water, the higher the ADPODS amount in the first rinsing solution. For any given rinsing method, the ADPODS amount in the second rinsing solution tended to slightly increase with increasing salinity. Interestingly, the ADPODS amount in the second rinsing solution was much lower than that in the first rinsing solution. Therefore, it can be concluded that most of surfactant remaining on the fabric surface was removed by the first rinse.

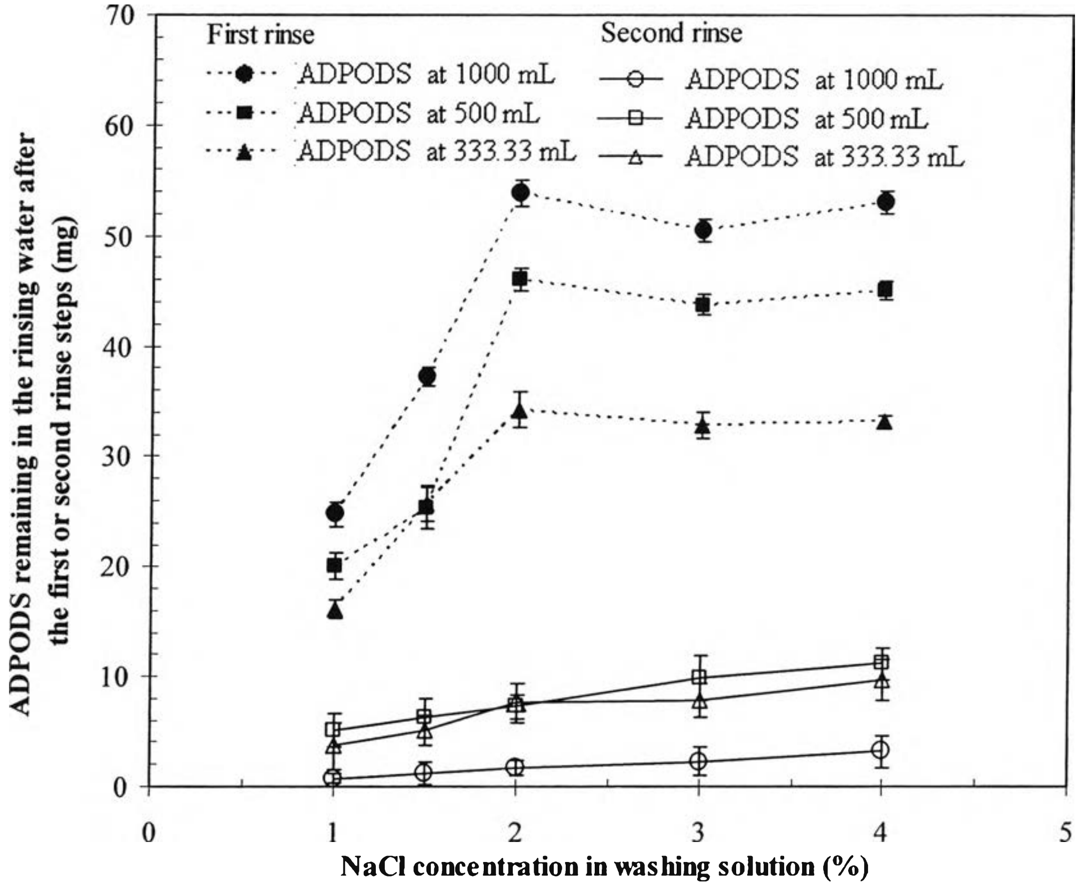

Figure 5.11 The ADPODS remaining in the rinsing water after the first or second rinse steps at various salinities and different amounts of rinsing water.

The percentage of ADPODS remaining in each rinsing solution based on the initial amount of ADPODS (70 mg) and the oil removal as a function of salinity are shown comparatively in Figure 5.12. As mentioned earlier, the ADPODS amount in the first rinsing solution at different amounts of rinsing water showed similar trends. For any given quantity of rinsing water, the higher the ADPODS amount in both first and second rinsing solutions, the higher the total oil removal. The results reveal that the residual surfactants adsorbing on the fabric surface during the wash step subsequently came off with the rinsing water during the rinse step. Interestingly, a very high ADPODS amount in the rinsing solution appeared when the salinity was greater than 1.5% and the maximum ADPODS removal from the fabric surface was found at the optimum salinity of 2% (see Figure 5.12a).

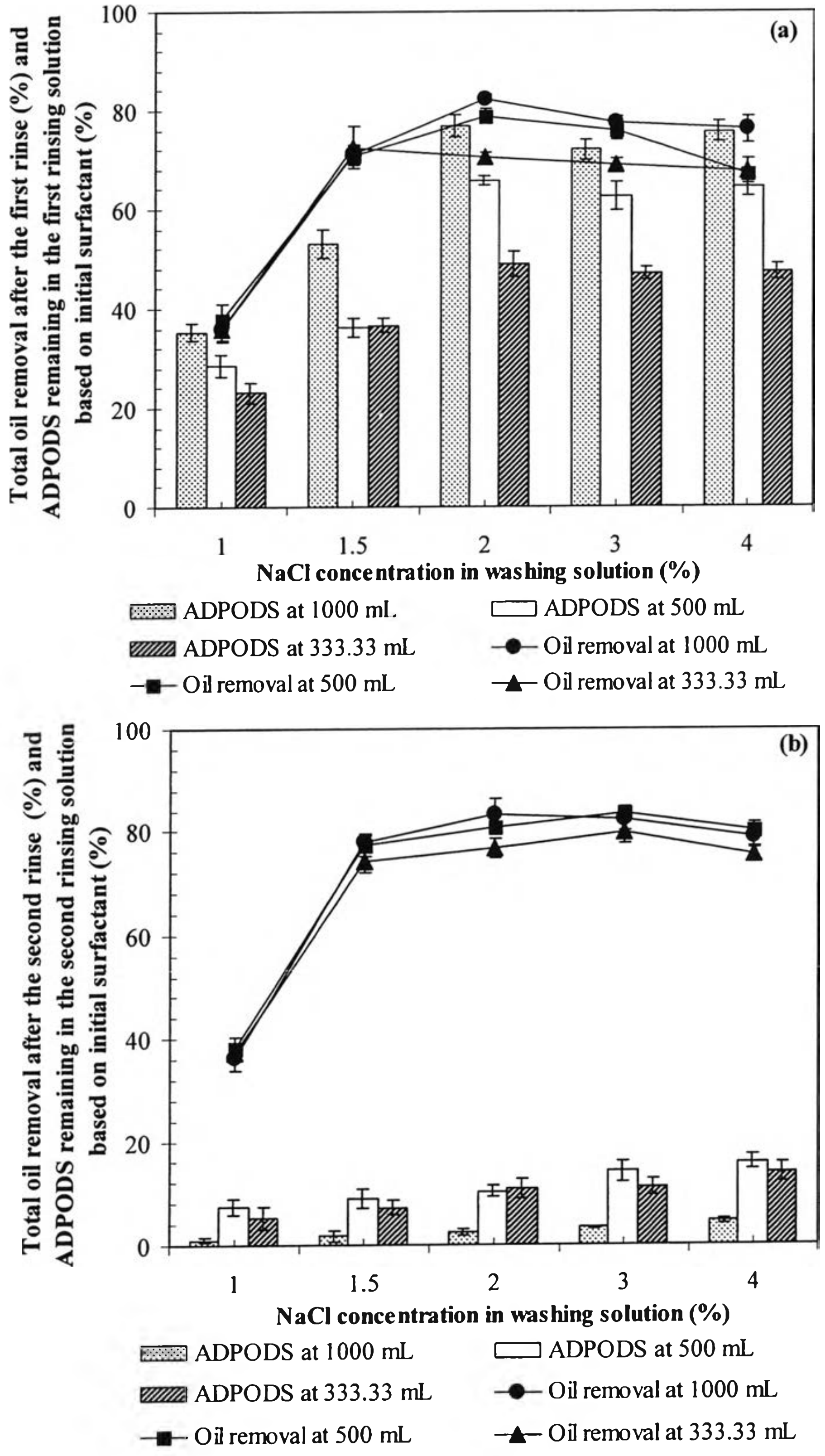

Figure 5.12 The amount of ADPODS left in different rinse steps and the total oil removal after (a) the first rinse (b) the second rinse at different amounts of rinsing water.

Moreover, it was observed that the ADPODS amount in the rinsing solution decreased with decreasing amount of rinsing water for the first rinse. As expected, the percentage of ADPODS amount remaining in the second rinsing solution based on the initial ADPODS (70 mg) was found to be much lower than that in the first rinsing solution, indicating that most of residual ADPODS on the fabric surface came out during the first rinse. The ADPODS amount in the second rinsing solution decreased with increasing the volume of rinsing water which was different from the results in the first rinse step. It can be explained in that a higher quantity of rinsing water simply enhances the removal of the residual surfactants on the fabric surface specially in the first rinse step, leading to lowering the residual surfactants.

From the results as shown in Figures 5.10-5.12, the surfactants adsorbing on the attached oil and fabric surfaces during the wash step are believed to be a crucial factor affecting the detergency performance. During the wash step, the surfactants adsorb onto both the fabric and the attached oil, resulting in decreasing the IFT between the oil and the bath, as well as increasing the contact angle between the attached oil and the fabric surface. The higher the surfactant adsorption, the higher the possibility of oil detachment from the fabric. However, an increase in the surfactant adsorption will decrease the surfactant concentration in the washing solution, resulting in decreasing the solubilization capacity in the washing bath. This explains why the oil removal decreases with increasing residual surfactants on the fabric and/or soil surface, as shown in Figure 5.9. During the rinse step, the surfactant desorption simply increases the solubilization capacity of the system, as indicated by the increasing oil removal. The higher the surfactant adsorption in the wash step, the higher the oil removal in the rinse step (see Figure 5.6).

In this study, the percentages of residual ADPODS on the fabric surface after the first and second rinses at different rinsing methods calculated based on the initial weight of ADPODS and based on the 100 g fabric are shown in Figure 5.13.

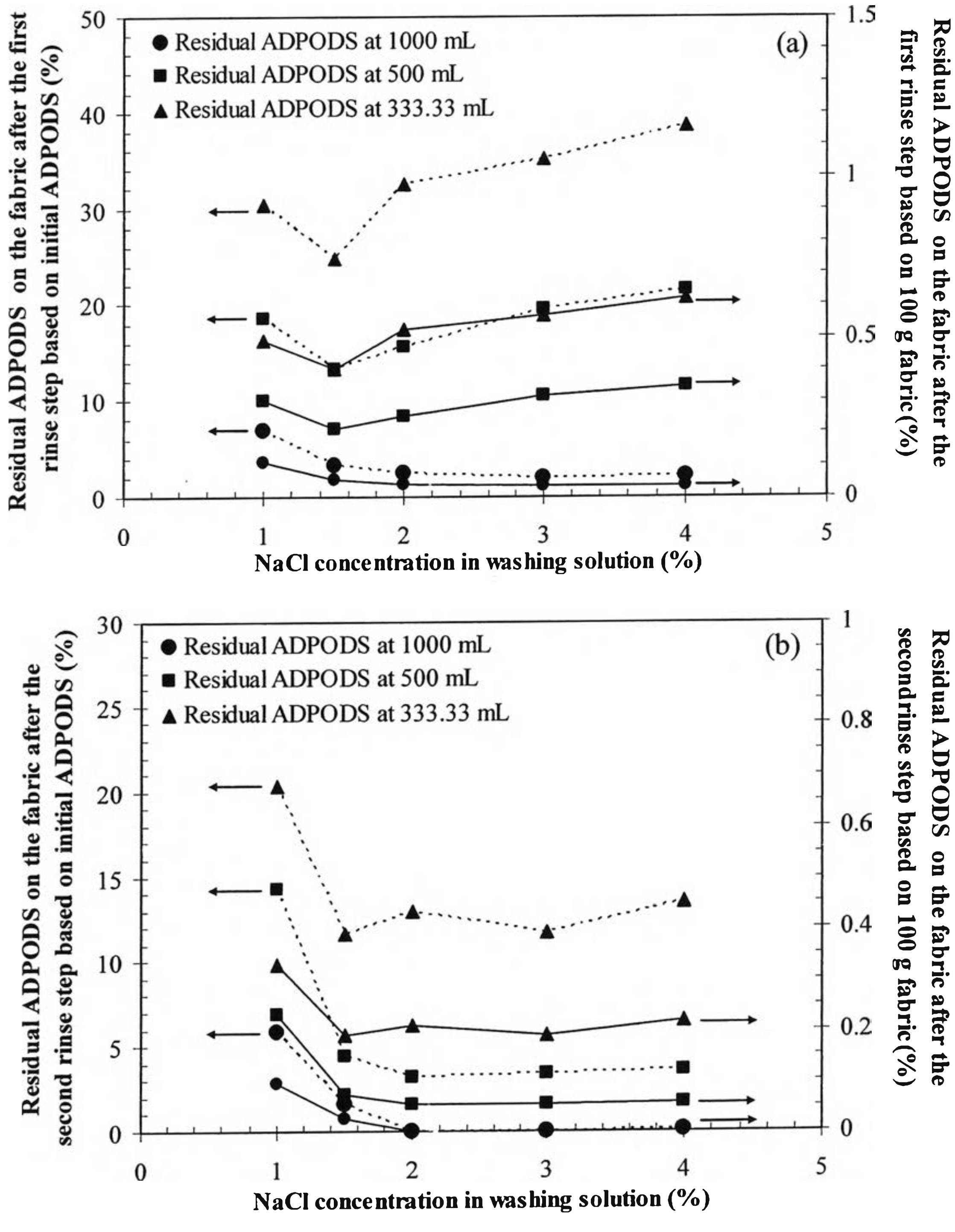

Figure 5.13 The percentage of residual ADPODS on the fabric surface at different rinse methods based on the initial ADPODS and 100 g fabric (a) after first rinse and (b) after second rinse.

For any given rinsing method, the residual ADPODS on the fabric surface after the first rinse was greater than that after the second rinse. The residual ADPODS was almost zero at salinity greater than 2% with 2 rinses of 1000 mL volume. As expected, the system with 333.33 mL rinsing water showed the highest amount of residual ADPODS on the fabric for both rinses. Interestingly, at the supersolubilization condition (1.5% salinity). From the results, it can be concluded that the higher the volume of rinsing water used, the lower the residual ADPODS on fabric.

For any given rinsing method, the residual surfactants after the second rinse decreased with increasing NaCl concentration and reached a minimum at the optimum salinity. An important objective of the rinse step is to remove the residual surfactants on the fabric for preventing skin irritation. Then, the selected formulation at the optimum conditions with a low amount of rinsing water might not be appreciated because of the presence of a quite high amount of residual surfactants on the fabric, even though it shows very high detergency performance. As shown in Figures 5.12 and 5.13, an increase in salinity clearly increases both the detergency performance in terms of high oil removal as well as low residual surfactants, suggesting that optimum salinity should be considered as one of important process parameter in oily soil detergency.

Moreover, the present results also showed a lowest amount of rinsing water (333.33 mL) with 2 rinses was sufficient to achieve high oil removal. As mentioned before, the main purpose of the rinse step is to remove the residual surfactants adsorbing on the fabric surface which may cause skin irritation. In order to investigate the amount of the residual surfactants after the washing, additional experiments were conducted with an unsoiled fabric at the optimum conditions. Figure 5.14 shows the residual ADPODS in each step in terms of percentage based on the initial ADPODS amount (70 mg) at different rinsing methods with the selected formulation at the optimum conditions as compared to the unsoiled fabric.

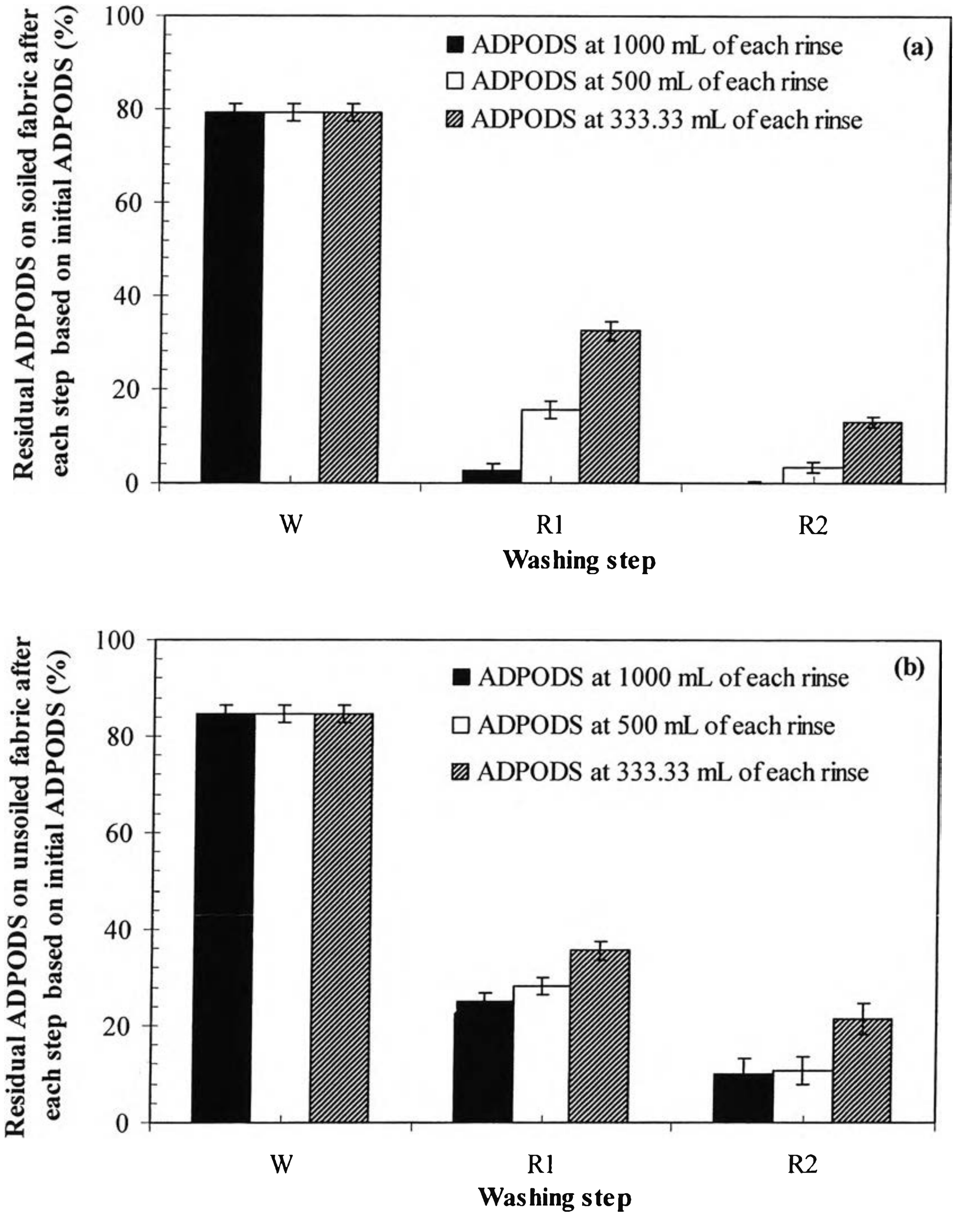

Figure 5.14 The residual ADPODS on fabric in each step based on the initial ADPODS amount (a) on the soiled fabric (b) on unsoiled fabric at different rinsing methods under the selected formulation (1:10:6 of ADPODS:AOT:Span 80) with the optimum salinity and at 30 °C.

For the case of the soiled fabric, a large portion of ADPODS upto 80% still remained on the fabric surface after the wash step and most of the residual ADPODS was removed in the first rinse. The results showed that the higher the volume of rinsing water, the lower the residual ADPODS. Interestingly, at the highest quantity (1000mL) of rinsing water, the residual ADPODS with two rinses approached zero. For the case of unsoiled fabric, the residual ADPODS on the fabric surface in each step had a similar trend. In comparisons between the soiled and unsoiled fabrics, the residual ADPODS on the fabric surface was found to be similar for these two cases. However, the residual ADPODS on the unsoiled fabric was significantly higher than that on the soiled fabric after rinsing. The result can be explained in that the unsoiled fabric is more hydrophilic, leading to a higher ADPODS adsorption on the unsoiled fabric than that on the soiled fabric.

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5.6 References

1. Scamehorn JF, Sabatini DA, Harwell JH (2004) Surfactants, Part II: Applications In: Atwood JL, Steed JW (eds) Encyclopedia of Supramolecular Chemistry. Marcel Dekker, New York, pp 1470-1476
2. Verma S, Kumar VV (1998) Relationship between Oil-Water Interfacial Tension and Oily Soil Removal in Mixed Surfactant Systems. J Colloid Interface Sci 207: 1-10
3. Rosen MJ (2004) Surfactants and Interfacial Phenomena, Wiley, New York
4. Benton WJ, Raney KH, Miller CA (1986) Enhanced Videomicroscopy of Phase Transitions and Diffusional Phenomena in Oil-Water-Nonionic Surfactant Systems. J Colloid Interface Sci. 110: 363-388
5. Raney KH, Benton WJ, Miller CA (1987) Optimum Detergency Conditions with Nonionic Surfactants: I Ternary Water Surfactant-Hydrocarbon Systems. J Colloid Interface Sci 117: 282-290
6. Raney KH, Benson HL (1990) The Effect of Polar Soil Components on the Phase Inversion Temperature and Optimum Detergency Conditions. J Am Oil Chem Soc 67: 722-729
7. Raney KH (1991) Optimization of Nonionic/Anionic Surfactant Blends for Enhanced Oily Soil Removal. J Am Oil Chem Soc 68: 525-531
8. Bidyut KP, Satya PM (2001) Uses and Applications of Microemulsions. Curr Sci India 80: 990-1001
9. Tongcumpou C, Acosta EJ, Quencer LB, Joseph AF, Scamehorn JF, Sabatini DA, Chavadej S, Yanumet N (2003) Microemulsion Formation and Detergency of Oily Soils: I Phase Behavior and Interfacial Tension. J Surfactants Deterg 6: 191-203
10. Tongcumpou C, Acosta EJ, Quencer LB, Joseph AF, Scamehorn JF, Sabatini DA, Chavadej S, Yanumet N (2003) Microemulsion Formation and Detergency of Oily Soils: II Detergency Formation and Performance. J Surfactants Deterg 6: 205-213
11. Tongcumpou C, Acosta EJ, Quencer LB, Joseph AF, Scamehorn JF, Sabatini DA, Chavadej S, Yanumet N (2005) Microemulsion Formation and

Detergency of Oily Soils: III Performance and Mechanisms. J Surfactants Deterg 8: 147-156

12. Dörfler HD, Grosse A, Krüssmann H (1996) The Use of Microemulsions as Cleaning Media. Tenside Surfactants Deterg 33: 432-440
13. Azemar N (1996) The Role of Microemulsions in Detergency Process. In: Solans C, Kunieda H (eds) Industrial Applications of Microemulsions. Marcel Dekker, New York, pp 375-387
14. Rybinski WV (2002) Surface Chemistry in Detergency. In: Holmberg K, Shah DO, Schwuger MJ (eds) Handbook of Applied Surface and Colloid Chemistry, John Wiley & Sons, West Sussex, UK, pp 53-72
15. Tanthakit P, Chavadej S, Scamehorn JF, Sabatini DA, Tongcumpou C (2007) Microemulsion Formation and Detergency with Oily Soil: IV Effect of Rinse Cycle Design. J Surfactants Deterg (Accepted January, 2008)
16. Graciaa A, Lachaise J, Cucuphat C, Bourrel M, Salager JL (1993) Improving Solubilization in Microemulsions with Additives. 1. The Lipophilic Linker Role. Langmuir 9: 669-672
17. Graciaa A, Lachaise J, Cucuphat C, Bourrel M, Salager JL (1993) Improving Solubilization in Microemulsions with Additives. 2. Long-Chain Alcohol as Lipophilic Linkers. Langmuir 9: 3371-3374
18. Acosta E, Uchiyama H, Sabatini DA, Harwell JH (2002) The Role of Hydrophilic Linkers. J Surfactants Deterg 5: 151-157
19. Acosta E, Uchiyama H, Tran S, Sabatini DA, Harwell JH (2002) Formulating Chlorinated Hydrocarbon Microemulsions Using Linker Molecules. Environ Sci Technol 36: 4618-4624
20. Acosta EJ, Mellisa LA, Harwell JH, Sabatini DA (2003) Coalescence and Solubilization Kinetics in Linker-Modified Microemulsions and Related Systems, Langmuir 19: 566-574
21. Salager JL, Graciaa A, and Lachaise J (1998) Improving Solubilization in Microemulsions with Additives. Part III: Lipophilic Linker Optimization. J Surfactants Deterg 1: 403-406

22. Uchiyama HE, Acosta E, Sabatini DA, Harwell JH (2000) Supersolubilization in Chlorinated Hydrocarbon Microemulsions: Solubilization Enhancement by Lipphilic and Hydrophilic Linker. Ind Eng Chem Res 39: 2704-2708
23. Salager JL, Miñana-Perez M, Pérez-Sénchez M, Ramirez-Gouveia M, Rojas CI (1983) Surfactant-Oil-Water Systems near the Affinity Inversion Part III: The Two Kinds of Emulsion Inversion. J Dispersion Sci Technol 4: 313-329
24. Miñana-Perez M, Jarry P, Pérez-Sénchez M, Ramirez-Gouveia M, Salager JL (1986) Surfactant-Oil-Water Systems near the Affinity Inversion Part V: Properties of Emulsions. J Dispersion Sci Technol 7: 331-343
25. Salager JL (2000) Emulsion Properties and Related Know-how to Attain Them. In: Nielloud F, Marti-Mestres G (eds) Pharmaceutical Emulsions and Suspensions. Marcel Dekker, New York, pp 73-125
26. Standard Guide for Evaluating Stain removal Performance in Home Laundering, Annual Book of ASTM Standards, Vol.15.04, American Society for Test and Materials, West Conshohocken, PA, 2000, ASTM D 4265-98.
27. Goel SK (1998) Measuring Detergency of Oily Soils in the Vicinity of Phase Inversion Temperatures of Commercial Nonionic Surfactants Using an Oily-Soluble Dye. J Surfactants Deterg 1: 221-226
28. Wu B (1996) Formulation of Petroleum Microemulsions Systems for Surfactant Enhanced *in-situ* Subsurface Remediation. M.S. Thesis. University of Oklahoma, Norman, p.15.
29. Huh C (1979) Interfacial Tensions and Solubilizing Ability of a Microemulsion Phase that Coexists with Oil and Brine. J Colloid Interface Sci 71: 408-426
30. Salager JL (200) Formulation Concepts for the Emulsion Maker. In: Nielloud F, Marti-Mestres G (eds) Pharmaceutical Emulsions and Suspensions. Marcel Dekker, New York, pp 19-72
31. Kegel WK, Lekkerkerker HNW (1993) Competition between a Lamellar and a Microemulsion Phase in an Ionic Surfactant System. J Phys Chem 97: 11124-11133
32. Bastogne S, David C (1998) Quaternary N-alkylaldonamide-Brine-Decane-Alcohol System Part I: Phase Behavior and Microemulsions. Colloids Surf A 139: 311-320

33. Lee JM, Lim KH (2004) Changes in Morphology of Three-Phase Emulsions with Temperature in Ternary Amphiphile/Oil/Water Systems. Colloids Surf A 248: 57-65
34. Lee JM, Lim KH (2005) Changes in Two-Phase Emulsion Morphology in Temperature-Amphiphile Concentration or Fish Diagram for Ternary Amphiphile/Oil/Water Systems. Colloids Surf A 290: 241-249
35. Queste S, Salager JL, Strey R, Aubry JM (2007) The EACN Scale for Oil Classification Revisited Thanks to Fish Diagrams. J Colloid Interface Sci 312: 98-107
36. Acosta EJ, Harwell JH, Sabatini DA (2004) Self-Assembly in Linker Modified Microemulsions. J Colloid Interface Sci 274: 652-664