



## CHAPTER IV

### MICROEMULSION FORMATION AND DETERGENCY WITH OILY SOIL: IV EFFECT OF RINSE CYCLE DESIGN

#### 4.1 Abstract

The objective of this work was to apply a microemulsion-based formulation for removal of motor oil in laundry detergency at low salinity. To produce the desired phase behavior, three surfactants were used: alkyl diphenyl oxide disulfonate (ADPODS), sodium dioctyl sulfosuccinate (AOT) and sorbitan monooleate (Span 80). The mixed surfactant system of 1.5% ADPODS, 5% AOT and 5% Span 80 (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80 of the total actives) was found to form a middle phase microemulsion (Type III) at a relatively low salinity of 2.83% NaCl. When this formulation was diluted, detergency performance increased with increasing total surfactant concentration and leveled off above about 0.1% total actives on the three types of fabrics studied (pure cotton, 65/35 polyester/cotton blend, and pure polyester). Detergency was found to improve with increasing hydrophilicity of the fabric with cotton being cleanest after washing and polyester the most difficult to clean. To achieve a specified oil removal, less rinse water can be used if a higher number of lower-volume rinses are employed. An interesting characteristic of microemulsion-based formulations is that a substantial fraction of oil removal occurs during the rinse cycle. In this work, this removal is shown to be due to the low oil/water interfacial tension during initial rinsing and is therefore strongly correlated to residual surfactant concentration in the rinse steps. As a result, the number of rinses and the volume of water per rinse can profoundly affect detergency in these systems.

**Key words:** Detergency, microemulsion, mixed surfactants, motor oil, rinse water

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## 4.2 Introduction

Detergency of oily soil, is a complex dynamic process that is affected by several factors such as interfacial tension (IFT) of the system, time, washing temperature, hydrodynamic force exerted during the wash process, the surface characteristics of substrates, additives (e.g., builders, enzymes, antideposition agents), water hardness, etc [1-3]. In detergency, the term “soil” can be classified into three categories: particulates (solid, usually inorganic), oils (liquid, usually organic), and stains (unwanted dyestuffs) [4]. Oily soil is among the most difficult to remove. Due to the great variabilities inherent in the substrates and oily soils, detergency cannot be described by a single mechanism but rather involves a number of different and potentially simultaneous mechanisms, depending on the nature of the substrate and the oily soil [5].

Several mechanisms can cause oily soil removal, including roll-up, snap off, and emulsification-solubilization. The roll-up mechanism is facilitated by an increase in contact angle exhibited between the oil droplet and the substrate as a result of the washing solution [2]. Other mechanisms such as solubilization-emulsification are believed to play an important role in the detergency process as well [5,6]. Low or ultralow oil/water IFT and high solubilization can result from the presence of microemulsions in the system. The correlation between microemulsion formation and detergency has been noted in a number of studies [1, 7-16]. It has been shown that the maximum detergency corresponds to the optimum conditions of the system where the minimum oil/water IFT of the microemulsion exists [7,16,17]. Both surfactant concentration and composition are crucial to attaining ultralow IFT. For a nonionic surfactant system, the optimum occurs at the phase inversion temperature (PIT). In a system with ionic surfactants, the salt concentration at optimum, which is known as the optimum salinity, produces minimum IFT [18].

Hydrophilic and lipophilic linkers are molecules which can decrease the rigidity and increase the thickness, respectively, of the interfacial layer between the oil and water phases which can result in more rapid microemulsion formation and lower oil/water IFT in microemulsion systems [19-23]. In our previous studies [13-15], formulation of mixed surfactants based on the linker concept were used to form

microemulsions with both motor oil and hexadecane in detergency studies. The three surfactants used, in decreasing order of hydrophilicity, were: alkyldiphenyloxide disulfonate (ADPODS), sodium dioctyl sulfosuccinate (AOT), and sorbitan monooleate (Span 80). The mixture of these three surfactants exhibited both ultralow IFT and relatively high solubilization with both oils studied [13]. For this primarily anionic surfactant system, as salinity increases, the system transitions from a Winsor Type I to III to II microemulsion. In a Type I system, the surfactant is mostly in a water phase in equilibrium with an excess oil phase. In a Type III system, a third or middle phase containing the surfactant is in equilibrium with a water and an oil phase. In a Type II system, the surfactant is present mostly in the oil phase in equilibrium with an excess water phase. Minimum IFT values are observed in a Winsor Type III system, with optimum conditions producing the lowest IFT within the Type III region. The supersolubilization region, which is in Winsor Type I microemulsion close to the transition zone between Winsor Type I and Winsor Type III microemulsion regions, achieved oil removal almostly as high as that for a Winsor Type III system [14]. In addition, under similar conditions, the detergency mechanisms were proposed to correlate the oil removal to the spreading effect related to the wettability of oil and substrate [15].

In previous studies, the optimum salinity was found to be 16% NaCl [13], which is quite high for this primarily anionic surfactant system of 3% AOT, 2% ADPODS and 2% Span 80. As a consequence, in this follow up study, the surfactant composition was adjusted in an effect to reduce this optimum salinity based on the linker concept of microemulsion formation with motor oil.

From previous work, in both the supersolubilization and middle phase regions, the oil removal in the rinse step was found to be as high as that in the wash step, in contrast to the commercial detergent where soil removal occurs predominantly in the wash step [14]. In order to further evaluate this unique aspect of microemulsion-based detergency, in this study we relate soil/water IFT to soil removal during the rinse step as well as study the effect of different rinse volumes and number of rinses on soil removal.

### 4.3 Experimental Procedures

#### 4.3.1 Materials

Alkyl diphenyl oxide disulfonate (ADPODS) or Dowfax 8390 was obtained as a 36% solution from Dow Chemical Co. (Midland, MI, USA). Dioctyl sodium sulfosuccinate (Aerosol-OT or AOT) with 98% purity was purchased 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 pure polyester, pure cotton and a polyester/cotton blend (65/35) were purchased from Test Fabrics Co. (Middlesex, NJ, USA).

#### 4.3.2 Phase Studies

Phase studies were performed by first adding an aqueous surfactant solution to flat-bottom-screw-cap tubes. Then, the studied motor oil was added to the aqueous surfactant solution to achieve a volumetric ratio of unity. The aqueous surfactant solutions added were prepared with different concentrations of three surfactants (ADPODS, AOT and Span 80) and NaCl. In this study, both surfactant and NaCl concentrations are reported in weight% based upon the aqueous phase. All vials containing the mixtures were well shaken for 3 min and placed in an incubator to equilibrate at 30 °C for approximately one month. After equilibration, the height of each liquid phase was measured using a cathetometer having a high precision of  $\pm 0.01$  mm. The solubilization capacities were calculated in terms of the solubilization parameter, which is the volume of either motor oil or water dissolved per gram of total surfactants. The IFT values between the two equilibrated phases were measured by a spinning drop tensiometer (Krüss, SITE 04).

#### 4.3.3 Surface Tension Measurements

The surface tension of surfactant solutions was determined by the DuNouy ring technique using a tensiometer (Krüss, K10T). All surface tension measurements were controlled at 30 °C.

#### 4.3.4 Fish Diagram Study

The types of microemulsion of the fish diagram were classified by the visual observation for the surfactant concentration greater than 0.8%. At the total surfactant concentration lower than 0.8%, a condition which is often not clearly visually observed, conductivity and IFT measurements were used to evaluate the microemulsion type. The measurement of electrolytic conductivity is one approach that can be used to determine the microemulsion type [24,25]. For each condition, the electrolytic conductivity was measured, under gentle stirring with a magnetic stirrer, by using a conductivity meter (Cyberscan model 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  $\mu\text{s/cm}$ ) [26]. The conductivity and the IFT results were used to plot the phase diagram or 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.

#### 4.3.5 Fabric Pretreatment and Soiling Procedures

Pre-washing of test fabrics was done to eliminate the residues of mill-finishing agents. The pre-washing method followed the ASTM standard guide D4265-98 [27]. The tested motor oil was stained by the oil soluble Oil-Red-O dye using the standard method [28] before being applied on the fabrics. Approximately 0.1 g of the oil-soluble dye was added to 100 mL of the oil. The colored oil was filtered until clear of solids. The soiling procedure was done by diluting 10 mL of the clear dyed oil with dichloromethane to 100 mL. The fabric was folded and completely submerged in the dyed oil solution for 1 min. The soiled fabric was then unfolded and laid on a flat plate in a ventilated hood at room temperature overnight in order to dry the soiled fabric. Then the dried soiled fabric was cut into 3×4 inch swatches in warp and weft directions. All swatches were freshly prepared for each batch of laundry experiments. By this soiling method, the average weight ratio of oil to fabric was approximately 0.21.

#### 4.3.6 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 1000 mL washing solution with 20 min washing time. Distilled water was used for rinsing. 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. One swatch was washed in each bucket and 3 replication experiments were performed for each experimental condition. 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.

#### 4.3.7 Oil Removal Measurements

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 reflectance using a UV/VIS Spectrophotometer (Hewlett Packard, 8452A), a procedure discussed by Goel [28].

#### 4.3.8 Dynamic IFT Measurements

Dynamic IFT measurements were carried out using a spinning drop tensiometer and a contact angle measurement analyzer by the drop shape analysis method (Krüss, DSA10 Mk2). 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.

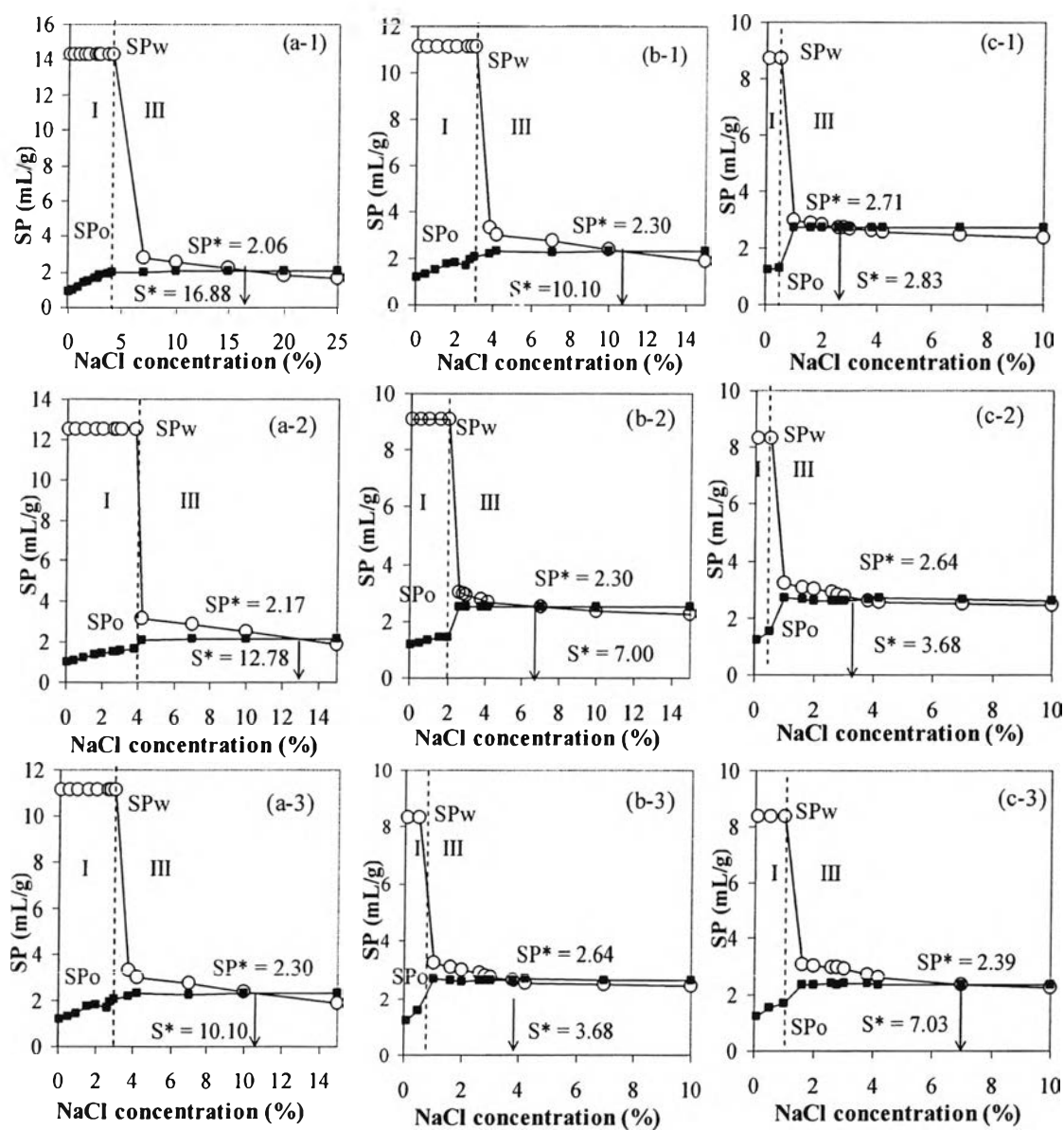
## 4.4 Results and Discussion

### 4.4.1 Effect of Surfactant Composition on Microemulsion Formation

To obtain a suitable formulation at low salinity for detergency application, each surfactant composition was varied while the other two surfactant concentrations were fixed. Based on our previous study [13], a mixture of 2% ADPODS, 3% AOT and 2% Span 80 was used as a starting composition in this study. SP is defined as the volume of oil solubilized (SP<sub>o</sub>) or of water solubilized (SP<sub>w</sub>) per weight of total surfactants in the microemulsion phase. Figure 4.1 illustrates the phase behavior of motor oil in terms of the solubilization parameters of water and oil (SP<sub>w</sub> and SP<sub>o</sub>) and the optimum salinity ( $S^*$ ) which occurs at the interception of SP<sub>w</sub> and SP<sub>o</sub>. At the  $S^*$  point, the solubilization parameter is known as the optimum solubilization parameter (SP<sup>\*</sup>) which is equal to SP<sub>w</sub> and SP<sub>o</sub> and where an equal volume of oil and of water are solubilized in the middle phase. The details of determining SP<sub>o</sub> and SP<sub>w</sub> values are explained elsewhere [13].

The more hydrophobic the surfactant used to form the microemulsion, the lower the optimum salinity of the system. Based on this understanding, the strategy to lower the optimum salinity of the surfactant blend is to increase the proportion of the hydrophobic surfactants, AOT (HLB = 10.2 in 1% brine) and Span 80 (HLB = 4.3) and to decrease the proportion of the hydrophilic surfactant, ADPODS (HLB > 40) [14]. Since the presence of the surfactants with widely different HLB values is generally necessary to form microemulsions without undesirable phase (e.g., gels, macroemulsion, or liquid crystal) or added alcohols at moderate temperatures, there are limits to permissible surfactant composition ranges.

In order to observe the effect of AOT concentration on microemulsion formation with motor oil, both ADPODS and Span 80 concentrations were fixed at 2% and the AOT concentration was varied from 3% to 5%. As shown in Figure 4.1 (a-1 to a-3), the higher the AOT concentration, the lower the optimum salinity of the system is. This is because of the lipophilic characteristic of AOT reduces the HLB of the system with increasing AOT concentration [29], and thus requires less salinity to reach the optimum point.



**Figure 4.1** 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) 2% ADPODS and 2% Span 80 were fixed, (a-1) 3% AOT, (a-2) 4% AOT and (a-3) 5% AOT; (b) 2% ADPODS and 5% AOT were fixed, (b-1) 2% Span 80, (b-2) 4% Span 80 and (b-3) 5% Span 80; (c) 5% AOT and 5% Span 80 were fixed, (c-1) 1.5% ADPODS, (c-2) 2% ADPODS and (c-3) 3% ADPODS. SP\* is SP at optimum salinity S\* where SP of oil (SPo) equals SP of water (SPw) into middle phase microemulsion phase.



Next, the ADPODS and AOT concentrations were fixed at 2% and at 5%, respectively, while the Span 80 concentration was varied from 2% to 5%: above 5%, separation of the aqueous phase occurred. The effects of the Span 80 concentration on solubilization parameters are illustrated in Figure 4.1 (b-1 to b-3). As the Span 80 concentration increased, the middle phase microemulsion (Winsor Type III) formed at a lower salinity and the optimum salinity was also lowered. The effect of increasing Span 80 concentration on the reduction of the optimum salinity was found to be greater than that of AOT because Span 80 is more hydrophobic than AOT.

Finally, the ADPODS concentration was varied from 1.5% to 3% while the concentrations of AOT and Span 80 were both kept constant at 5%. The lowest ADPODS concentration was limited to 1.5% since lower ADPODS concentration caused the system to become cloudy, indicating macroemulsion formation. From Figure 4.1 (c-1 to c-3), as the ADPODS concentration increases, a Winsor Type III microemulsion appears at a higher salinity and the optimum salinity also shifts to a higher value due to its high hydrophilicity of ADPODS [30].

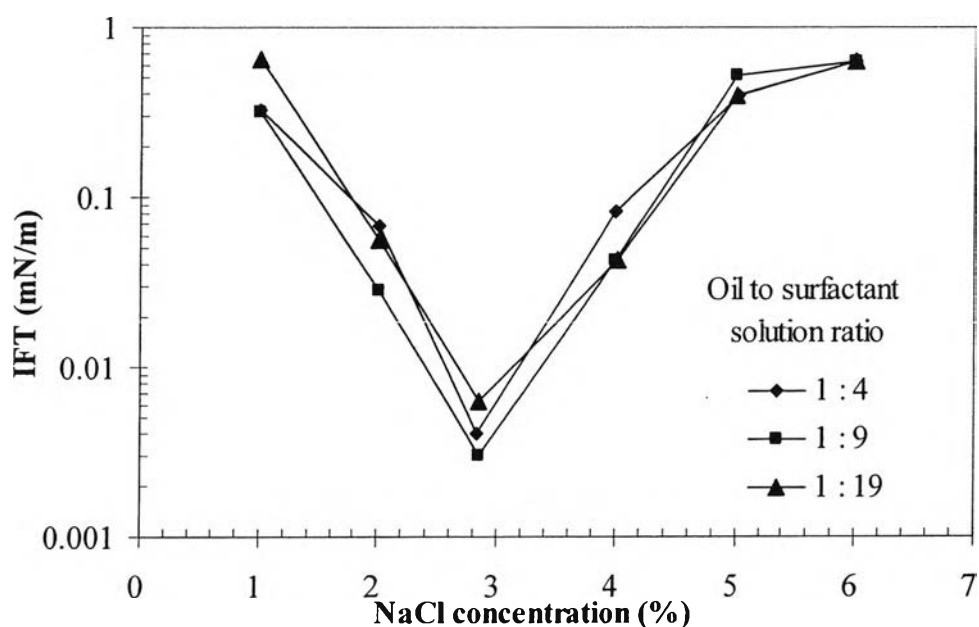
Based on these results, the formulation of 1.5% ADPODS, 5% AOT and 5% Span 80 which shows an optimum salinity of 2.83% was chosen for further study as compared to our previous formulation with a very high optimum salinity of 16% [13,14]. It should also be noted that this system has the highest SP value of the systems evaluated, which is encouraging relative to the efficiency of the chosen microemulsion system.

Since SP values are normalized to the amount of surfactant present, the difference in total surfactant concentration in these formulations used to study microemulsion formation (7 % in original vs. 11.5 % in new formulation) does not lead to confusion. But, it is important to note that the total surfactant concentration (total actives) in the laundering bath after dilution is approximately the same (0.115 vs. 0.1 %) between the two studies, so a fair comparison is being made.

#### 4.4.2 Effect of Oil-to-Surfactant Solution Ratio

In an actual detergency process, oil-to-surfactant solution ratios are generally much less than unity, unlike the one to one ratio normally used in most microemulsion phase studies including the present work. Due to preferential

partitioning of the different surfactant components into the bulk oil or water phases, the oil-to-surfactant solution ratio may affect the IFT of the system and thus the detergency performance [6,31]. The equilibrium IFT of the oil and surfactant solution at different oil-to-surfactant solution ratios and salinities is shown in Figure 4.2. Neither optimum salinity nor IFT at the optimum conditions were much affected by the studied range of oil-to-surfactant solution ratios. Interestingly, the optimum salinity and the minimum IFT were found experimentally to be independent of the oil-to-surfactant solution ratio. This implies that negligible concentrations of all three surfactants partition in the excess oil and water phases, since fractionation of the surfactant mixture is generally responsible for effects of oil-to-surfactant solution ratios on IFT and salinity at optimum conditions. Hence, phase behavior results obtained at 1:1 oil-to-surfactant solution ratio can be used to correlate with the detergency results operated at other oil-to-surfactant solution ratios.



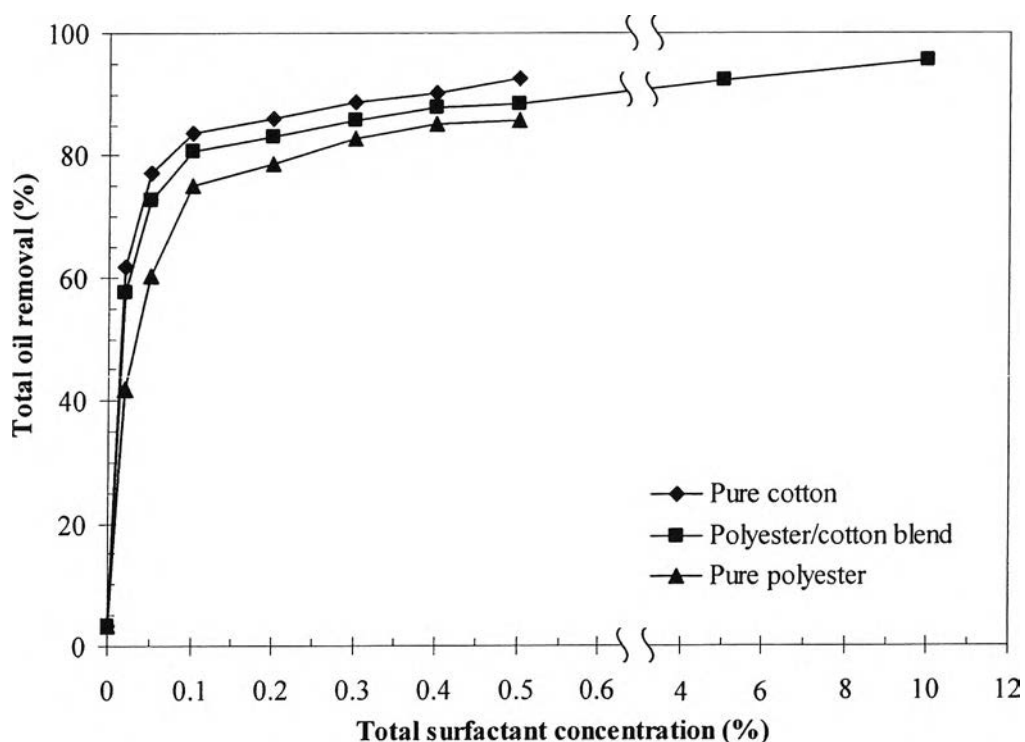
**Figure 4.2** Equilibrium IFT at different salinities and oil to surfactant solution volumetric ratios with the selected formulation (1.5% ADPODS, 5% AOT and 5% Span 80) at 30 °C.

#### 4.4.3 Effect of Surfactant Concentration on Detergency Performance

Figure 4.3 shows the oil removal as a function of total surfactant concentration on three types of fabrics using the selected formulation at the optimum

salinity. As shown in Figure 4.3, the oil removal increases with increasing total surfactant concentration and the system achieves the majority of its detergency by around 0.1% surfactant system for any tested fabric.

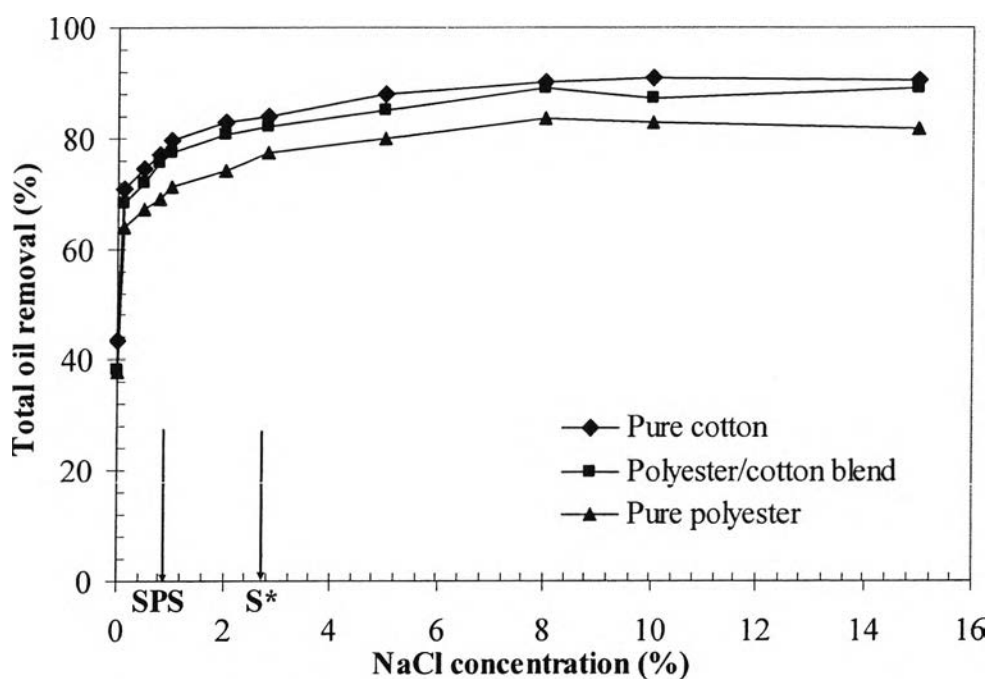
For any given total surfactant concentration, the oil removal on pure cotton was slightly higher than that on the other two types of fabrics and the lowest oil removal was found on the pure polyester. These results can be attributed to the hydrophobic surface of polyester having a much stronger interaction with the oil as compared to the hydrophilic surface of cotton. Therefore, it is more difficult to remove oily soil from polyester than from cotton which agrees with the results from Chi [32,33]. From these experiments, 0.115% surfactant concentration was selected for further detergency experiments.



**Figure 4.3** Effect of total surfactant concentration on oil removal at the optimum salinity (2.83%) with the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80).

#### 4.4.4 Effect of Salinity on Detergency Performance

Since the selected system contains a significant amount of the anionic surfactants (ADPODS and AOT), salinity can have a large effect on the system IFT, as shown in Figure 4.2. The effect of salinity on detergency performance was carried out in the washing experiments by varying NaCl concentration, whereas the total surfactant concentration was kept constant at 0.115% which was achieved by diluting a solution composed of 1.5% ADPODS, 5% AOT and 5% Span 80. So, the laundry wash solution was a 0.115 % surfactant solution of 13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80. Figure 4.4 shows the effect of salinity on the removal of motor oil on three types of fabrics.



**Figure 4.4** Effects of NaCl concentration on oil removal at different salinities with 0.115% total surfactant concentration of the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80) and two rinse steps.

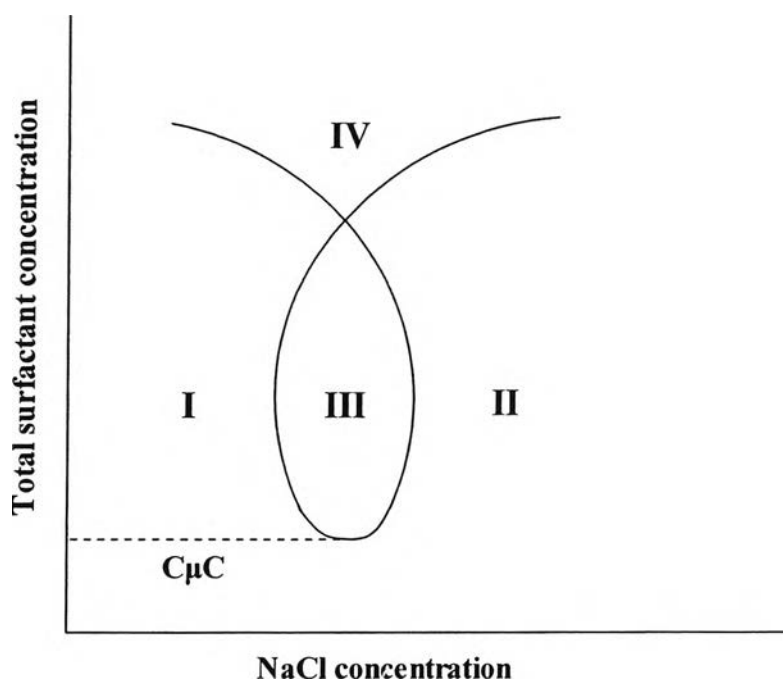
With increasing salinity of the system, the detergency performance improved significantly, especially at a very low salinity down to about 0.1% NaCl. Interestingly, the oil removal in the supersolubilization region (SPS) was found to be almost as high as that at the optimum region ( $S^*$ ). However, the oil removal increased slightly with increasing salinity higher than the optimum point for all types

of fabrics. These results are in good agreement with our previous studies [14]. Interestingly, for any given type of fabric, the maximum oil removal occurred at around 8% salinity which is much higher than the optimum salinity of 2.83% obtained from the phase studies, as shown in Figure 4.1. The result might be explained by the difference of the total surfactant concentration used in the phase studies and the detergency experiments. The total surfactant concentration in the phase studies was around 10 times of that in the detergency experiments since high concentrations are necessary to generate phase volumes large enough to measure.

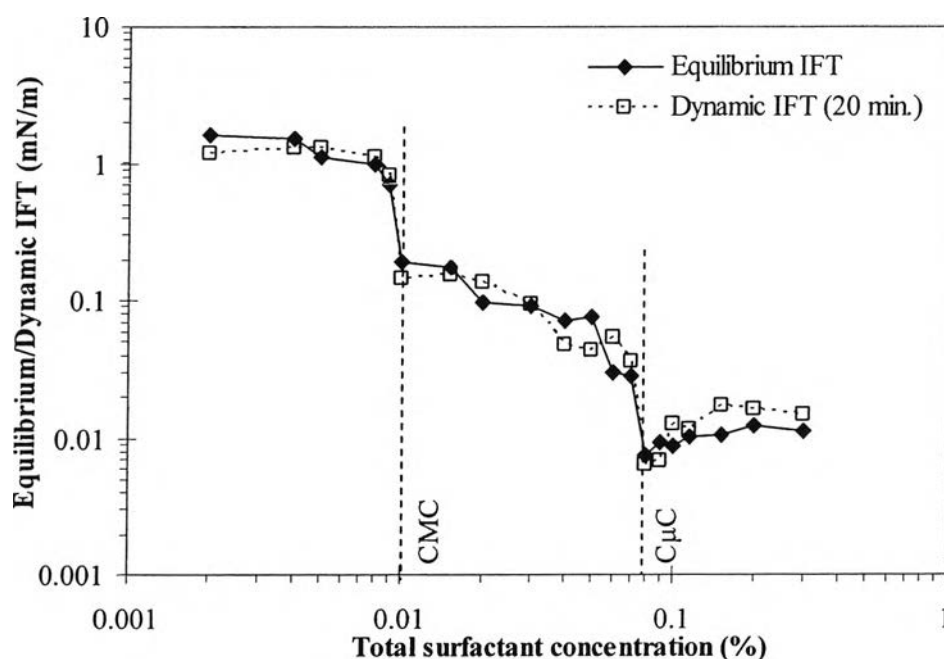
#### 4.4.5 Fish Diagram of Motor Oil with the Selected Formulation

The fish diagram has been used to describe the phase behavior of microemulsion systems for decades [34-39]. As shown schematically in Figure 4.5, 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 high surfactant concentration and corresponds to the whole solution being a single homogeneous surfactant-rich phase [35]. The phase diagram is shown as symmetrical in Figure 4.5, but could be tilted to the left or right. The lowest surfactant concentration at which the Type III microemulsion forms is known as the critical microemulsion concentration or  $C_{\mu C}$ , as shown in Figure 4.5; since the volume of the middle phase is too small to be visually observed at the  $C_{\mu C}$ , the surfactant concentration that first produce the ultralow IFT which is only attained when a Type III microemulsion is present. If the phase diagram is rotated  $90^\circ$ , it looks like a fish [34]. If a studied system consists of oil, water and nonionic surfactant, the role of salt or cosurfactant is replaced by temperature [37,38].

Since detergency is generally applied at a moderate surfactant concentration for cost reasons (0.115% for the present washing experiments), in the present work, the fish diagram was not investigated at very high surfactant concentrations, so the Type III to IV transition was not measured. In fact, the most important parameter from the fish diagram for this research is the  $C_{\mu C}$  since this is the minimum surfactant concentration needed to form a middle phase microemulsion.

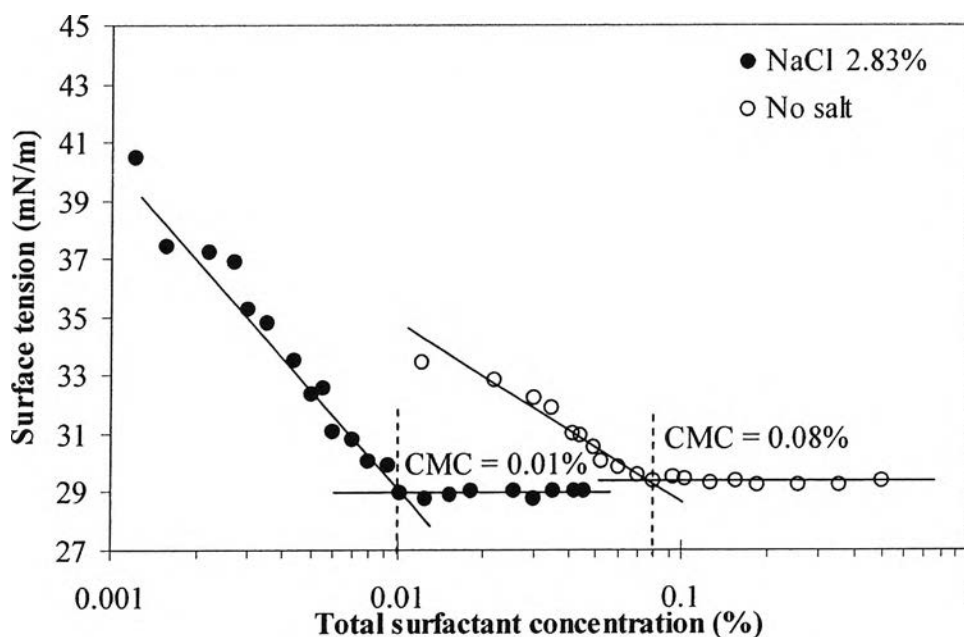


**Figure 4.5** Schematic representation of normal fish phase diagram. Roman numerals refer to the Winsor Type microemulsion existing at that condition.



**Figure 4.6** Equilibrium IFT and dynamic IFT at 20 min as a function of total surfactant concentration at 30 °C using the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80 with 2.83% NaCl).

In this study, the  $C_{\mu C}$  in the fish diagram was investigated by IFT measurement, as shown in Figure 4.6. It illustrates the IFT of an equilibrium system and dynamic system at 20 min as a function of total surfactant concentration at the optimum condition (2.83% salinity) of the selected formulation (a diluted sample of 1.5% ADPODS, 5% AOT and 5% Span 80 or 13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80 of the total actives). Both the 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. The first step corresponds to the adsorption of the surfactant at the oil-water interface, which occurs at concentrations less than the CMC. The second step 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 ( $C_{\mu C}$ ) [40]. From this observation, the CMC and  $C_{\mu C}$  were found at 0.01 and 0.08% of total surfactant concentration, respectively (Figure 4.6). The very sharp decrease in the IFT at the CMC and  $C_{\mu C}$  make determination of these values unambiguous as see in Figure 4.6.



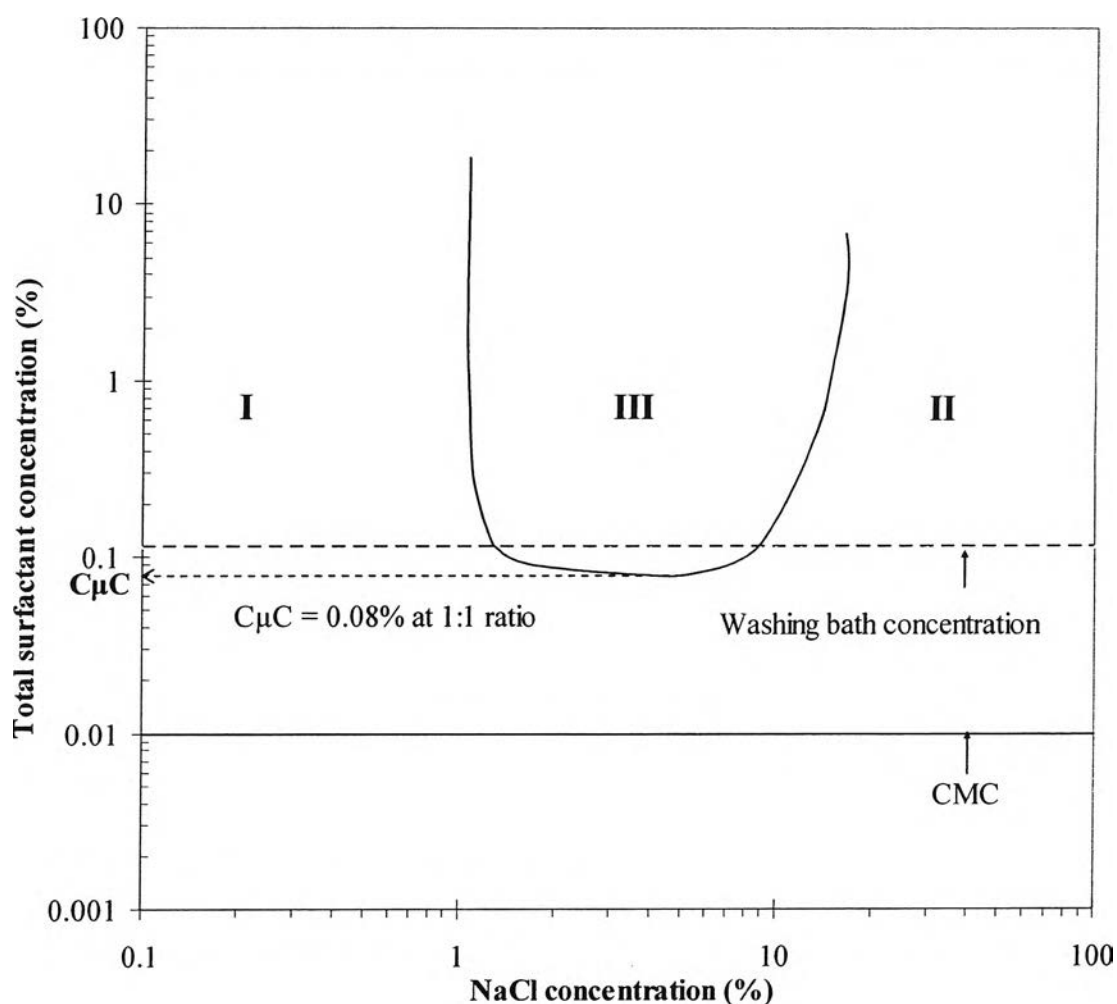
**Figure 4.7** Surface tension of the mixed surfactant system with and without salinity for the motor oil system

For comparisons of the equilibrium IFT and the dynamic IFT, equilibration time does not affect either values of the CMC and the  $C_{\mu}C$ s. Then, it is reasonably acceptable to apply the  $C_{\mu}C$  and the fish diagram for the conditions used in our washing experiments which was operated for 20 min of washing time. Figure 4.7 shows the equilibrium surface tension of the aqueous surfactant mixture used as the selected formulation with the salinity used (2.83% NaCl) and without salt. The CMC can be deduced from the surfactant concentration at which the plateau surface tension is first achieved [41]. The CMC (0.01%) deduced from the IFT data in Figure 4.6 is the same as that from the surface tension data in Figure 4.7 at 2.83% NaCl, which indicates that the solubilized motor oil does not significantly affect the CMC. This is reasonable for such nonpolar oil which solubilizes in the micelle core [5].

Figure 4.8 illustrates the fish diagram of our formulation at 1:1 oil-to-surfactant solution ratio. The fish diagram was constructed by using both the conductivity and IFT data. Surprisingly, a large area of the Winsor Type III was obtained as the head region of the fish diagram and the  $C_{\mu}C$  was found at a very low surfactant concentration of 0.08%. In this study, the transition from a Winsor Type III to a Winsor Type II microemulsions was observed at an extremely high salinity. Interestingly, the surfactant concentration (0.115%) in the washing bath used for the detergency experiment is located in the Winsor Type III region which is slightly higher than the  $C_{\mu}C$  (0.08%) and a much higher than the CMC (0.01%). Therefore, it can be noted that the diluted surfactant concentration used in the washing bath can still form the middle phase microemulsion and it also shows a high detergency performance (See Figure 4.3)

From Figure 4.3 at optimum salinity with varying surfactant concentration, there is only a modest increase in detergency with surfactant concentration above the total concentration (0.115 wt%) used for our base condition. Increasing the total surfactant concentration from slightly above the  $C_{\mu}C$  to approximately 2% total surfactant concentration or a factor of 25 increases oil removal from about 80% to 90%. Hence, it is unnecessary to increase the washing bath concentration much more than the  $C_{\mu}C$  to attain good detergency and there is no dramatic increase in detergency at the much higher concentrations than the  $C_{\mu}C$ .





**Figure 4.8** Fish phase diagram of our formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80) at an oil-to-water volumetric ratio of 1 to 1 at 30 °C.

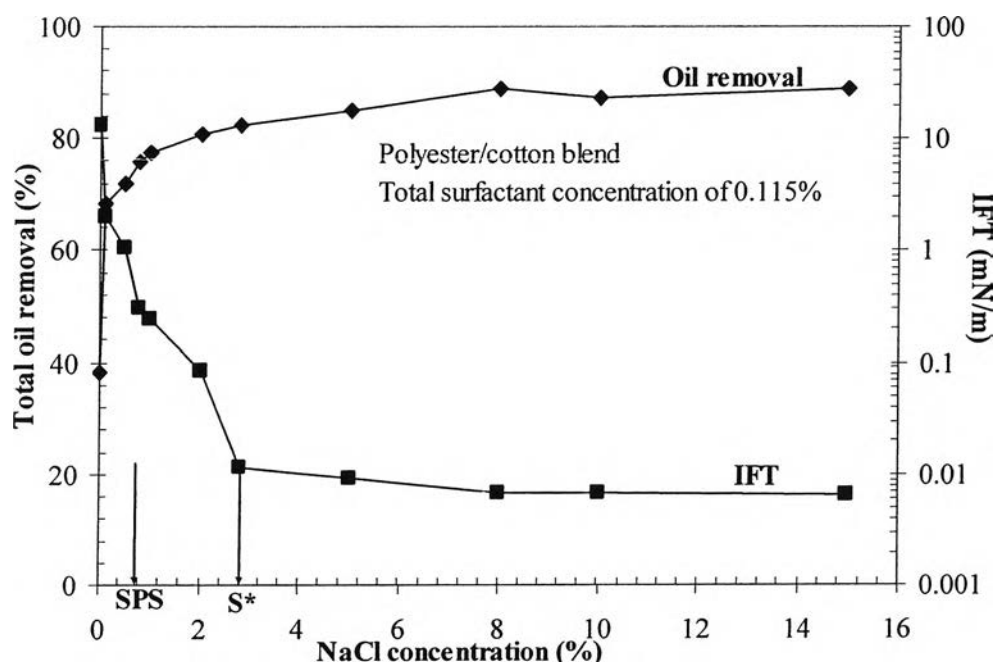
#### 4.4.6 Correlation of Microemulsion Formation and Detergency

##### Performance

The oil removal and equilibrium IFT between the washing solution and the dyed oil as a function of salinity are illustrated in Figure 4.9. A 0.115% total surfactant concentration for the selected formulation was used in the washing tests with the polyester/cotton blend as the fabric. As can be seen from Figure 4.9, the oil removal increases while the IFT decreases as salinity increases. The highest oil removal was found in the Winsor Type III region based on the phase study of the microemulsion formation at 1:1 oil-to-surfactant solution ratio (salinity > SPS) and

nearly plateaus above the optimum salinity ( $S^*$ ). The majority of improvement in oil removal with increasing salinity occurs prior to the SPS salinity, even though the IFT decreases greatly between the SPS (0.3067 mN/m) and optimum salinity ( $S^*$ ) (0.0114 mN/m). From these results, an IFT of around  $10^{-1}$  mN/m appears to be sufficient for excellent oily soil detergency and much lower IFT values only marginally increase detergency. Figure 4.9 and this hypothesis will be further discussed in the context of rinse cycle data later.

In our previous study with the same three surfactant blend and approximately the same concentration but in different proportions than here (2% ADPODS, 3% AOT and 2% Span 80 or 28.6 parts ADPODS, 42.9 parts AOT, and 28.6 parts Span 80 of the total actives), excellent detergency was observed, but the optimum salinity was much higher [13,14]. A goal of this study was to reformulate the surfactant mixture so lower and more practically feasible salinities could be used to achieve good oil removal. For example, the optimum salinity for the previous study was 16% NaCl, whereas in the current study it was 2.83% NaCl, while the SPS region occurs at 0.8% NaCl here where detergency is almost as good as at  $S^*$ .

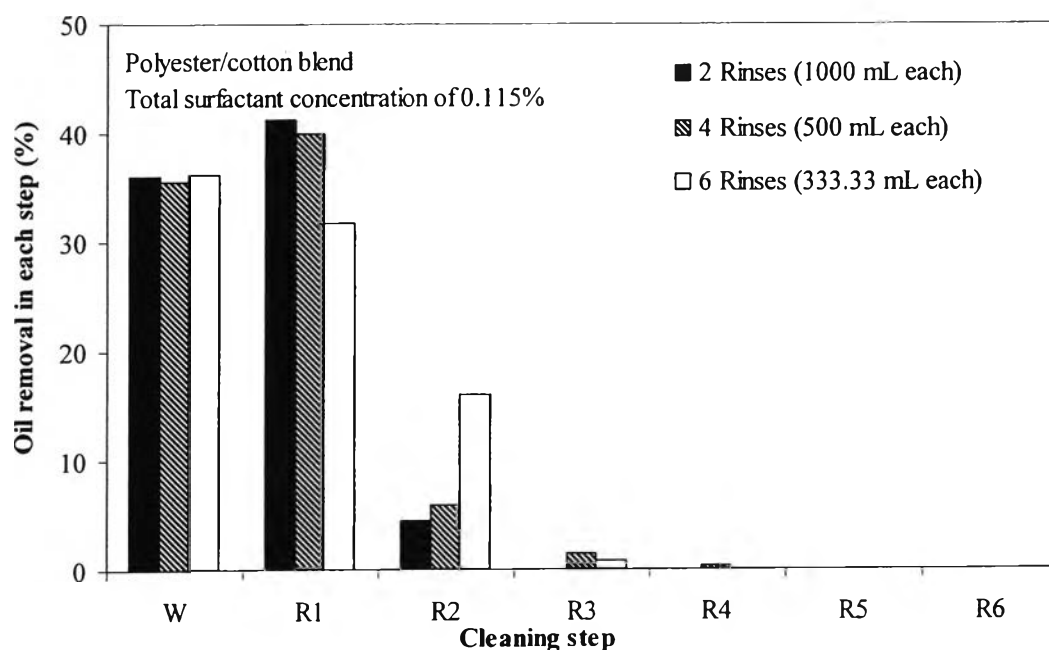


**Figure 4.9** Oil removal and equilibrium IFT between washing solution and oil as a function of salinity with the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80) and two rinses of 1000 mL each.

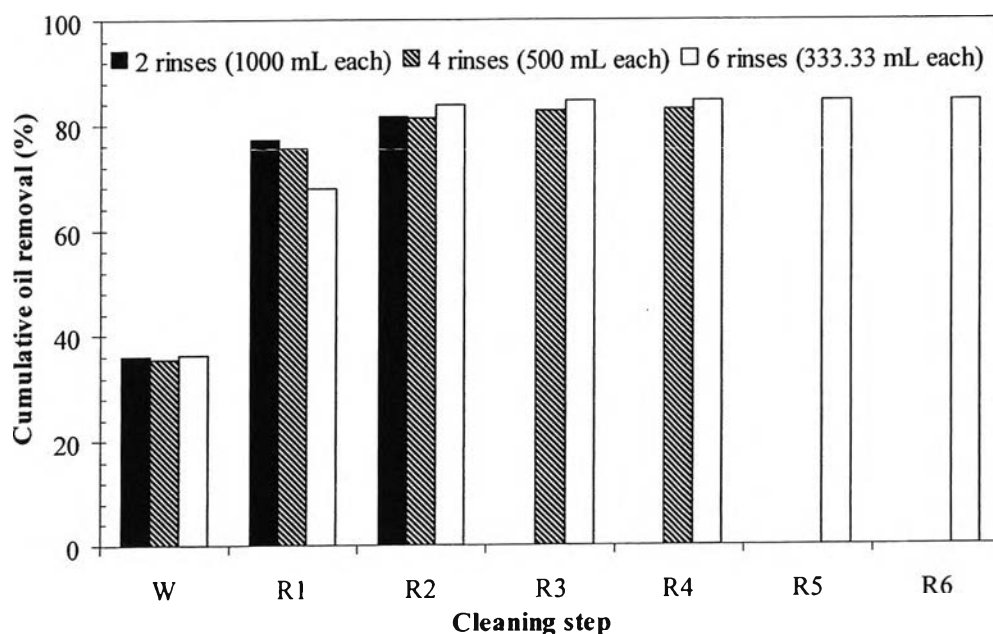
#### 4.4.7 Effects of Quantity of Rinsing Water and Number of Rinses on Oil Removal

One very peculiar characteristic of microemulsion-based detergency is that a substantial fraction of total oil removal (ca. half) occurs during the rinse steps, whereas in commercial liquid laundry detergents, oil removal is predominately in the wash step [14,15]. In real detergency practice, two rinses are commonly used. In our previous study of detergency experiments using two rinses, at both supersolubilization (SPS) and optimum ( $S^*$ ) regions where good detergency performance occurred, the oil removal during rinsing was found mainly in the first rinse [14,15]. In this present study, for better performance as well as water conservation purposes, the effects of the quantity of rinsing water and the number of rinse cycles were investigated. The wash step was performed with 0.115% total surfactant concentration of the selected formulation (1.5% ADPODS, 5% AOT and 5% Span 80 or 13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80 of the total actives) at the optimum salinity (2.83% NaCl). The washing test was done with 1000 mL of the washing solution for the wash step and a constant total quantity of rinsing water of 2000 mL distilled water for 2, 4 or 6 rinse steps. Therefore, 1000 mL, 500 mL and 333.33 mL of distilled water were used for each of 2, 4, 6 rinses, respectively. Each rinse within a cycle had the same volume of water.

The oil removal during each step in the detergency test with different rinse methods is illustrated in Figure 4.10. For any given method of rinsing, the oil removal in the first rinse (R1) was almost as high as that in the wash step (W) which is in good agreement with our previous study [14,15]. For the first or the second rinse (R1 or R2) using different volumes of rinsing water, the higher the quantity of rinsing water, a higher oil removal was obtained in the first rinse. In contrast, the higher the quantity of rinsing water, the lower the oil removal observed in the second rinse. Beyond the second rinse, the oil removal was very low for all cases. Therefore, oil removal is not improved by using rinses beyond two.



**Figure 4.10** Oil removal in each cleaning step with different volumes of rinsing water and different times of rinses using the selected formulation (W = the wash step ; R1= the first rinse ; R2 = the second rinse ; R3 = the third rinse and so on)

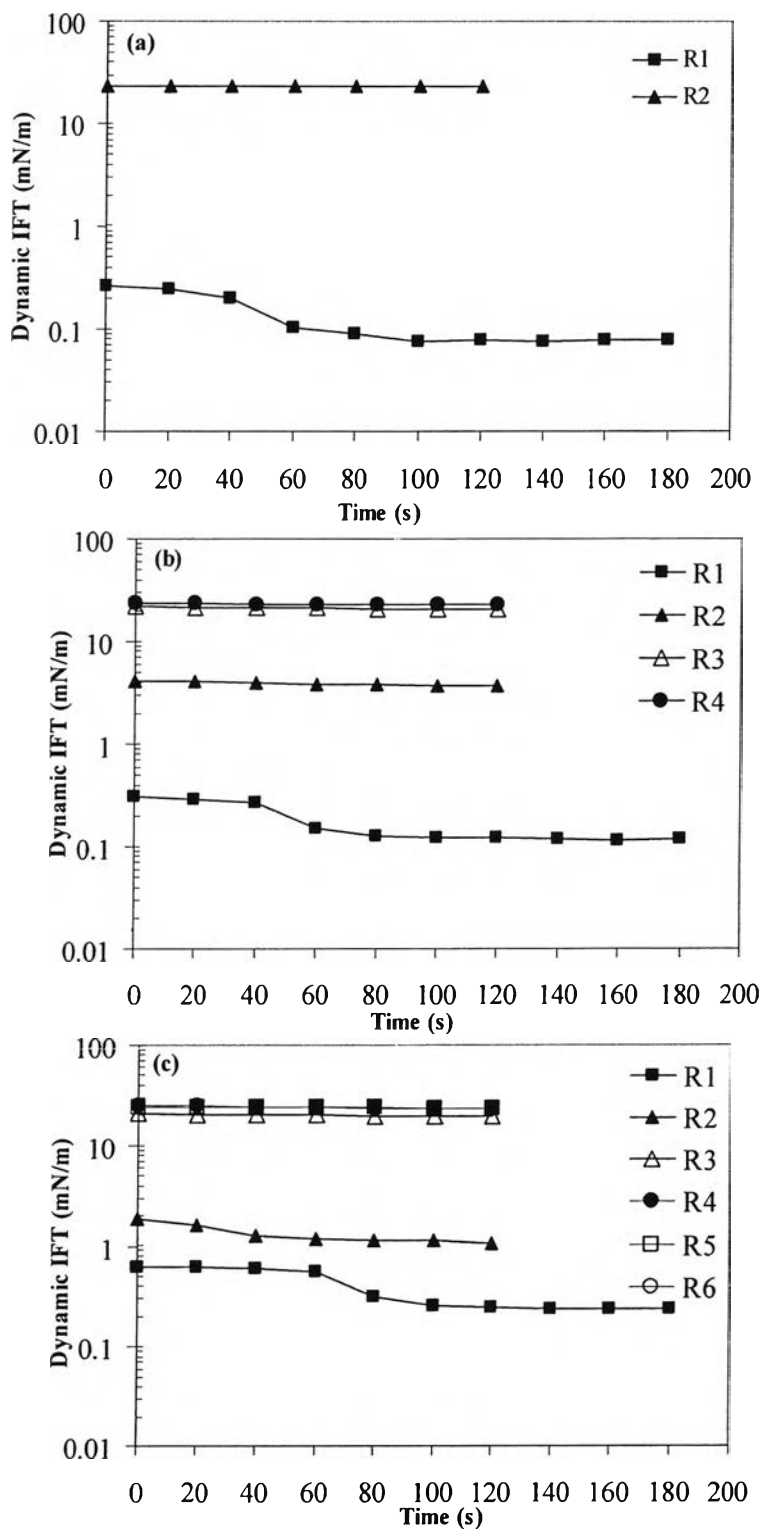


**Figure 4.11** Cumulative oil removal with different volumes of rinsing water and different numbers of rinse step using the selected formulation of total surfactant concentration of 0.115% (W = the wash step ; R1= the first rinse; R2 = the second rinse ; R3 = the third rinse and so on)

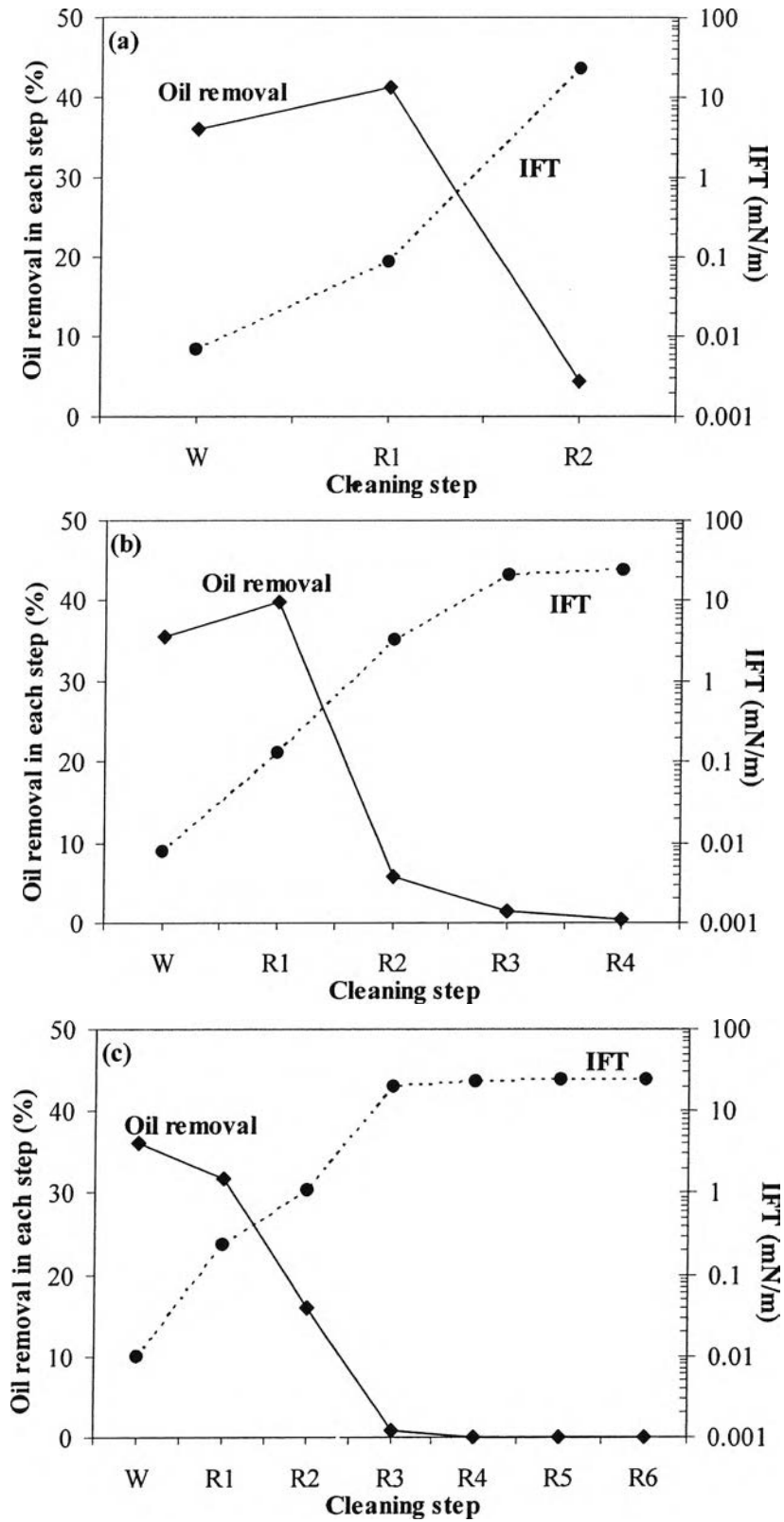
To observe the effect of quantity of rinsing water, the total oil removal (cumulative) at different volumes of rinsing water and different number of rinses is illustrated comparatively in Figure 4.11. The cumulative oil removal at the end of the three different rinsing processes was virtually independent of the number of rinse cycles.

The rinsing water after rinsing was collected to measure dynamic IFT with the dyed oil as shown in Figure 4.12. During rinsing, the adsorbed surfactant molecules onto the fabric surface as well as on the stained oil droplet desorbs into the rinsing water. Residual wash water trapped in the fabric also contributes surfactant to that in the rinse waters. For any given amount of rinsing water, a spontaneous dynamic IFT appears to plateau within 100 seconds, far shorter than a typical consumer washer rinse time.

As can be seen from Figure 4.12, both dynamic and equilibrium IFT increase with increasing number of rinses because of dilution. For any given quantity of rinsing water in the first rinse, the IFT value was still in the range of 0.1-0.2 mN/m which is clearly low enough to enhance oil removal. Since the wash step and at least the first rinse in detergency experiments were operated under ultralow IFT conditions, the mechanism of oil removal is likely dominated by the spreading effect in these steps, whereas the spreading effect is reduced during subsequent rinsing steps as described by Tongcumpou and coworkers [15].



**Figure 4.12** Dynamic IFT between rinsing water and dyed oil with the selected formulation and total surfactant concentration of 0.115%: (a) 2 rinses with 1000 mL each (b) 4 rinses with 500 mL each and (c) 6 rinses with 333.33 mL each



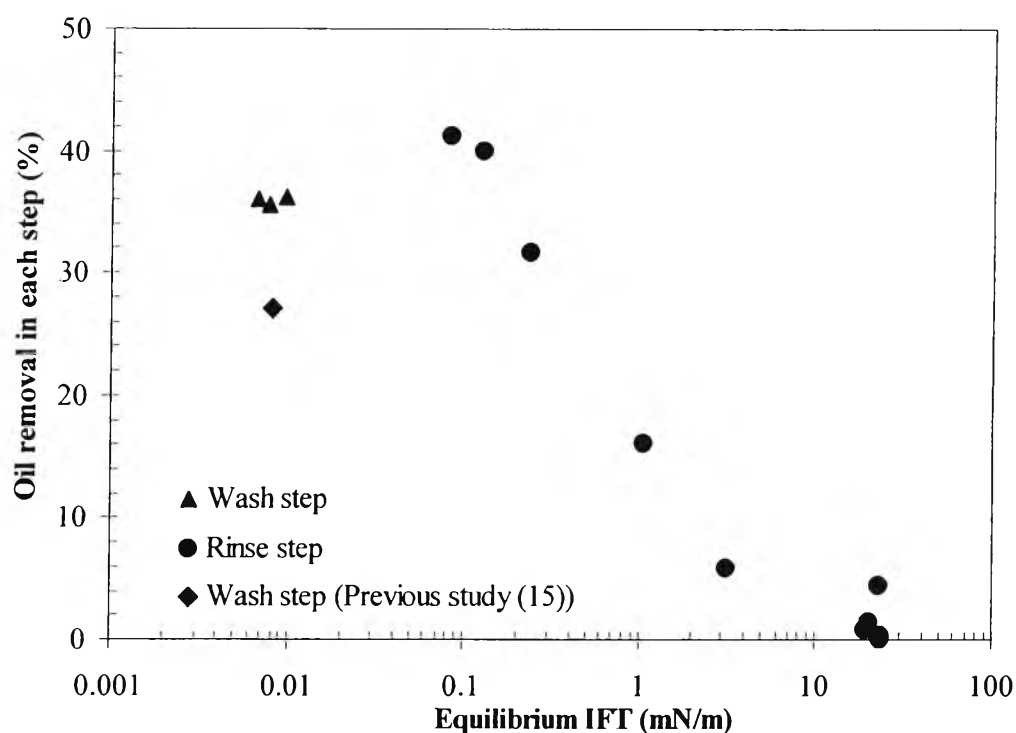
**Figure 4.13** Correlation of oil removal and equilibrium IFT in each step with the selected formulation and 0.115% total surfactant concentration: (a) 2 rinses with 1000 mL each (b) 4 rinses with 500 mL each and (c) 6 rinses with 333.33 mL each

#### 4.4.8 Correlation of Detergency Performance and Equilibrium IFT in the Rinse Step

As described earlier, the wash step had ultralow IFT ( $10^{-3}$ - $10^{-2}$  mN/m) using the studied formulation under the studied conditions. Hence, the oil removal in this step is believed to occur by emulsification-solubilization mechanism relating to an increase in the contact angle between the oil and the fabric. However, with a higher concentration of surfactants in the wash step, IFT is very low or ultralow, leading to spreading of oil droplets into fabric [15]. As a result, the oil can be partially removed during the wash step and further oil removal in the rinse step is as high as that in the wash step as confirmed by the present study and previous work [14,15]. The relationship between oil removal and IFT with different methods of rinsing is illustrated in Figures 4.13. As mentioned before, the IFT was very low (0.01 mN/m) during the wash step, leading to partial oil removal. For the first rinse, the IFT increased to be around 0.1 mN/m for all three methods of rinsing. The IFT decreased with increasing number of rinses because the surfactant concentration was lowered by the dilution effect. As can be seen in Figure 4.13, for any given rinsing method, a significant oil removal appears in the first rinse since the spreading effect is reduced, and therefore, the attached oil becomes droplets and eventually detaches from the fabric surface. However, after the second rinse or higher (R3, R4, R5 and R6), the IFT in the system became too high, resulting in decreasing contact angle.

Figure 4.14 illustrates oil removal in each step relating to the values of equilibrium IFT between washing (or rinsing) solution and oil with the selected formulation. As can be seen in Figure 4.14, during the wash step, the oil removal decreases with decreasing IFT below an IFT of about 0.1 mN/m. As explained above, the ultralow IFT in the wash step can result in the spreading effect to cause oil droplets to spread and penetrate into fabric surface, leading to low oil removal [15]. From the results, the maximum oil removal was obtained in the IFT range of 0.01 to 0.1 mN/m. For the IFT in the range of 0.1-5 mN/m, the oil removal decreased sharply. When the IFT of the system increased to values greater than 10 mN/m, there was almost no oil removal. This finding indicates that detergency performance is governed by the IFT of the system.





**Figure 4.14** Oil removal in each step related to the equilibrium IFT between washing (or rinsing) solution and oil with the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80).

From Figures 4.13 and 4.14, as long as the rinse water IFT is around 0.1 to 1.0 mN/m or lower, significant oil removal is observed in that rinse step, consistent with the hypothesis from our wash step results. In general, once a certain IFT is attained, lower IFT may not improve oil removal and at ultralow values can even reduce oil removal. More systems must be investigated to establish the generality of this observation, but the idea that the lower the IFT, the better for oily soil detergency seems invalid; reducing the IFT below a threshold value is sufficient to achieve excellent cleaning.

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