CHAPTER VI
MICROEMULSION FORMATION AND DETERGENCY OF OILY SOIL: VI. EFFECT OF WATER HARDNESS AND BUILDER

6.1 Abstract

In this study, the effects of water hardness and builder on both the phase diagrams of aqueous microemulsions with motor oil and the laundry detergency of oil removal from a polyester/cotton blend was investigated. Water hardness and builder were found to insignificantly affect the microemulsion phase diagram with motor oil. A mixed surfactant system of 0.1% $C_{14-15}(PO)_3SO_4Na$ and 5% $C_{12-14}H_{25-29}O(EO)_5H$ (2 parts $C_{14-15}(PO)_3SO_4Na$, and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$ of the total actives) at 4% salinity was used to study the effects of water hardness; the addition of any studied builder–sodium tripolyphosphate (STPP) or ethylenediaminetetraacetic acid (EDTA) – was found to have an insignificant effect on the oil removal. From the detergency results, the total oil removal decreased with increasing water hardness while the interfacial tension (IFT) increased. When hard water was used in laundering, the total oil removal was improved at a certain level, even though an excess amount of STPP or EDTA was added in the selected formulation.

Key words: Builder, detergency, water hardness, microemulsion, motor oil

6.2 Introduction

Detergency or the process of the soil removal, is a complex kinetic process. The effectiveness of detergency is dependent on many factors, such as the physical properties of the soil, the washing solution and fabrics, the washing time, temperature, and electrolyte level [1-3]. The quality of water also plays an important role in the success or failure of the washing process. Water hardness, which results from the presence of divalent cations mostly calcium and magnesium, is considered to be an important factor affecting the laundering [4-8]. Water hardness is measured in grains per gallon (gpg) or parts per million (ppm). Water containing less than 60 ppm hardness is considerably soft, whereas water with more than 180 ppm hardness is considered to be very hard [9,10].

Hard water affects laundering in several ways [10-12]. Incomplete soil removal normally occurs when hard water is used in laundering. Because of the remaining soil after washing, fabrics feel harsh and stiff. Moreover, washing with hard water requires a greater amount of detergent compared to the use of soft water since the divalent cations can react with the detergent to form a complex or precipitate. Hard water generally has a negative effect on the color appearance of fabrics, especially causing light colors and whites to become gray and dingy. In addition, washing with hard water can damage the fabric, shortening its life span. It has been found that calcium is in the fabric matrix when hard water is used in laundering [4]. Moreover, the residual calcium in the fabric results in making the fabric stiffer and more brittle, leading to increased friction and wear as the fabric flexes. In an effort to overcome the problems derived from water hardness, most commercial laundry detergents contain builders, whose purpose is to complex calcium and magnesium, making them less available to precipitate the anionic surfactants in the formulation [9]. Builders can be water-soluble or insoluble [12,13]. We study soluble builders here since they are primarily used in liquid detergents for which we have been developing formulations [14-17].

For decades, the relationship between microemulsion formation between an oily soil and water with detergency has been investigated [18-21] because microemulsions exhibit ultralow interfacial tension (IFT) at the oil/water interface and permits high oil solubilization [22]. It is known that maximum oily soil detergency performance corresponds to the optimum condition in the middle phase microemulsion, or Winsor Type III microemulsion region, which provides both the highest oil solubilization and lowest IFT [23]. Typically, the "optimum" condition can be obtained at the lowest IFT value or the interception point between the solubilization parameters of oil and water. The solubilization parameter (SP) is defined as the volume of either oil or water dissolved per unit weight of total surfactant. The use of microemulsion-based formulations was found to provide better oil removal in the washing process than a typical commercial liquid laundry detergent [14-17].

In this work, the effects of water hardness and added builder on the laundry detergency of motor oil with a microemulsion-based formulation was studied.

6.3 Experimental Procedures

6.3.1 Materials

Branched alcohol propoxylate sulfate sodium salt with three PO groups ($C_{14-15}(PO)_3SO_4Na$) was provided by Sasol North America Inc. (Lake Charles, LA) in a 28.6% solution. Secondary alcohol ethoxylate (SAE or $C_{12-14}H_{25-29}O(EO)_5H$) in a 100% solution, Tergitol 15-S-5, was purchased from Utica Chemical Co. Ltd., the supplier of Dow Chemical in Thailand. Analytical grade NaCl, $CaCl_2$, and $MgCl_2$ were purchased from LabScan Asia Co, Ltd. Motor oil that is commercially available for use in gasoline engines, type SAE 10W-30 (Castrol GTX), was used as a model oily soil. Since the motor oil used in this research is a commercial product and can vary in composition, the same batch of oil was used throughout this research. Oil red O (solvent Red 27, CI. No. 26125) was purchased from Aldrich Chemical Company, Inc. Sodium tripolyphosphate (STPP) was supplied by Thai Polyphosphate & Chemicals Co. Ltd. Ethylenediaminetetraacetic acid (EDTA) was supplied by Dow Chemical Co. A commercial liquid detergent

(Unilever, Breeze Excel), available in the Thailand market, which contains 4% sodium linear alkybenzene sulphonate, 2% ethoxylate alcohol, and 8.5% sodium lauryl ether sulphate was also used in detergency experiments. Dichloromethane and 2-propanol, analytical reagent grade, were purchased from LabScan Asia Co, Ltd. All chemicals were used as received without further purification. Standard unsoiled fabric (65/35 polyester/cotton blend) was purchased from Test Fabrics Co. (Middlesex, NJ, USA). Deionized water was used throughout this research for preparing aqueous surfactant solutions and rinsing water.

6.3.2 Phase Studies

The phase behavior of the microemulsions was measured using a salinity scan at a 1:1 volumetric ratio of water to motor oil and 30 °C. In this study, the stated concentration of surfactants and NaCl are weight percentages based on the aqueous phase. The details of the procedure for microemulsion preparation were described in our previous work [14-17]. To investigate the effect of water hardness on microemulsion formation, aqueous surfactant solutions were prepared with different degrees of water hardness (0, 100, 500, 1000 ppm). Water hardness was simulated here by using $CaCl_2$ and $MgCl_2$ at a Ca^{2+}/Mg^{2+} molar ratio of 3:2. The mixture in each vial was shaken well for 3 min and left in an incubator, for the attainment of equilibrium, at 30 °C for one month. After equilibration, the height of each liquid phase was measured by using a cathetometer (Titan Tool Supply, TC-II) attached to a digimatic height gauge (Mitutoyo, 192-631) with a precision of ± 0.01 mm. Then, the solubilization parameters (SP), as mL of either oil or water dissolved in the phase predominantly containing the surfactant per unit weight (g) of total surfactants, were calculated [12].

In this work, the types of microemulsions were identified by visual observation for total surfactant concentrations greater than 0.6%. At a total surfactant concentration lower than 0.6%, conductivity and equilibrium IFT measurements were used to determine the types of microemulsions since visual observations are ambiguous in this region. Electrolytic conductivity can be used to determine the microemulsion type [24,25] and in this study, the electrolytic conductivity was measured, under gentle stirring with a magnetic stirrer, by using a conductivity meter (Cyberscan, con110). Since the aqueous phase contains NaCl, the inversion is easily monitored by a change of two or more orders of magnitude in conductivity (ms/cm or µs/cm) [26]. Apart from the visual observation at high surfactant concentrations, the conductivity and the equilibrium IFT results were used to plot the phase diagram, or the conditions where Winsor Type I, II, and III microemulsions exist.

6.3.3 Surface Tension Measurement

The surface tension of the 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) [27].

6.3.4 Dynamic IFT Measurement

Dynamic IFT measurements were also carried out using a spinning drop tensiometer (Krüss, SITE 04) at 30 °C. The heavy phase was the aqueous surfactant solution, and the light phase was the dyed oil. A volumetric ratio of 100:1 aqueous solution-to-oil was used to measure IFT values.

6.3.5 Fabric Preparation and Soiling Method

The testing fabric (polyester/cotton blend) 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 [28]. The studied motor oil was dyed by the oil soluble Oil-Red-O dye using the standard method [29] 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. After being soaked for 1 min, the fabric was then unfolded and laid on a flat plate in a ventilated hood to dry at room temperature overnight in order to remove the dichlomethane solvent. 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 laundry experiments.

6.3.6 Laundry Procedure

Detergency experiments were carried out by using a tergotometer (Copley, DIS 8000), which 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 at an agitation speed of 110 rpm. The first rinse took 3 min, while the second rinse step took 2 min with 1000 mL rinsing water per rinse. The washing solution was prepared at different total surfactant and NaCl concentrations using the selected formulation. The rinsing water had the same water hardness level used in the washing solution and without added NaCl. All experiments were carried out at a constant temperature of 30 °C. Three soiled swatches were washed together for one cycle as replicants. In addition, the commercial grade detergent was also used at different total surfactant concentrations without salt in order to compare the detergency performance with the selected formulation. In order to determine the effect of added builders, a washing solution having 0.3% total surfactant concentration and different degrees of water hardness was prepared at different molar ratios of builder-to-water hardness.

6.3.7 Oil Removal Measurement

Oil removal is characterized by the portion of attached oil on the swatches that is washed out during the detergency process. The residual 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) according to the procedure given by Goel [29]. The difference of the amount of extracted oil before and after laundering is used to indicate the oil removal efficiency in this study.

6.3.8 Analysis of Water Hardness

The amount of free divalent cations of the solution samples was determined by the tritration method with EDTA (ethylenediaminetetraacetic acid) as the titrant and Eriochrome Black T (Erio T) as the indicator [30].

6.4 Results and Discussion

6.4.1 Effect of Surfactant Composition on the Microemulsion Phase Diagram

Since three different salts are being added to the systems in this work (NaCl, $CaCl_2$ and $MgCl_2$), all at variable concentrations, must be taken in the use of terminology. The electrolyte concentration being systematically varied to induce formation of the different microemulsion types (e.g. Winsor Type I, II, or III) and IFT values associated with them is generally called salinity and the results of such phase studies is called salinity scans. In this work, that electrolyte is NaCl. Electrolytes which simulates water hardness ($CaCl_2$ and $MgCl_2$) were set at any constant total concentration for a set of experiments where a salinity scan was performed. Therefore, in accordance with the convention in microemulsion phase studies, salinity in this work refers to NaCl concentration.

The SP is defined as a volume of oil solubilized (SPo) or of water solubilized (SPw) per weight of total surfactant in the microemulsion phase. In the study of the microemulsion phase diagram with motor oil, SPw and SPo were determined by using the phase height measurement, and the optimum salinity (S*) was obtained at the interception of SPw and SPo. At the S* point, the solubilization parameter is known as the optimum solubilization parameter (SP*), which coincides with the equal solubilization capacity of oil and water. In this study, $C_{14-15}(PO)_3SO_4Na$ and $C_{12-14}H_{25-29}O(EO)_5H$ were selected to form microemulsions with motor oil. These two surfactants were used in this research instead of the three mixed surfactant formulations in our previous work [14-17] because one component (alkyl diphenyl oxide disulfonates, ADPODS) of the mixed surfactant system has unacceptable biodegradation rates for some applications. To form microemulsions of motor oil with $C_{14-15}(PO)_3SO_4Na$ and $C_{12-14}H_{25-29}O(EO)_5H$, in this study, the concentration of each surfactant was varied while the concentration of the other surfactant was kept constant. Firstly, the $C_{14-15}(PO)_3SO_4Na$ concentration was varied in the range of 0.1 to 1% while the $C_{12-14}H_{25-29}O(EO)_5H$ concentration was fixed at 5%.

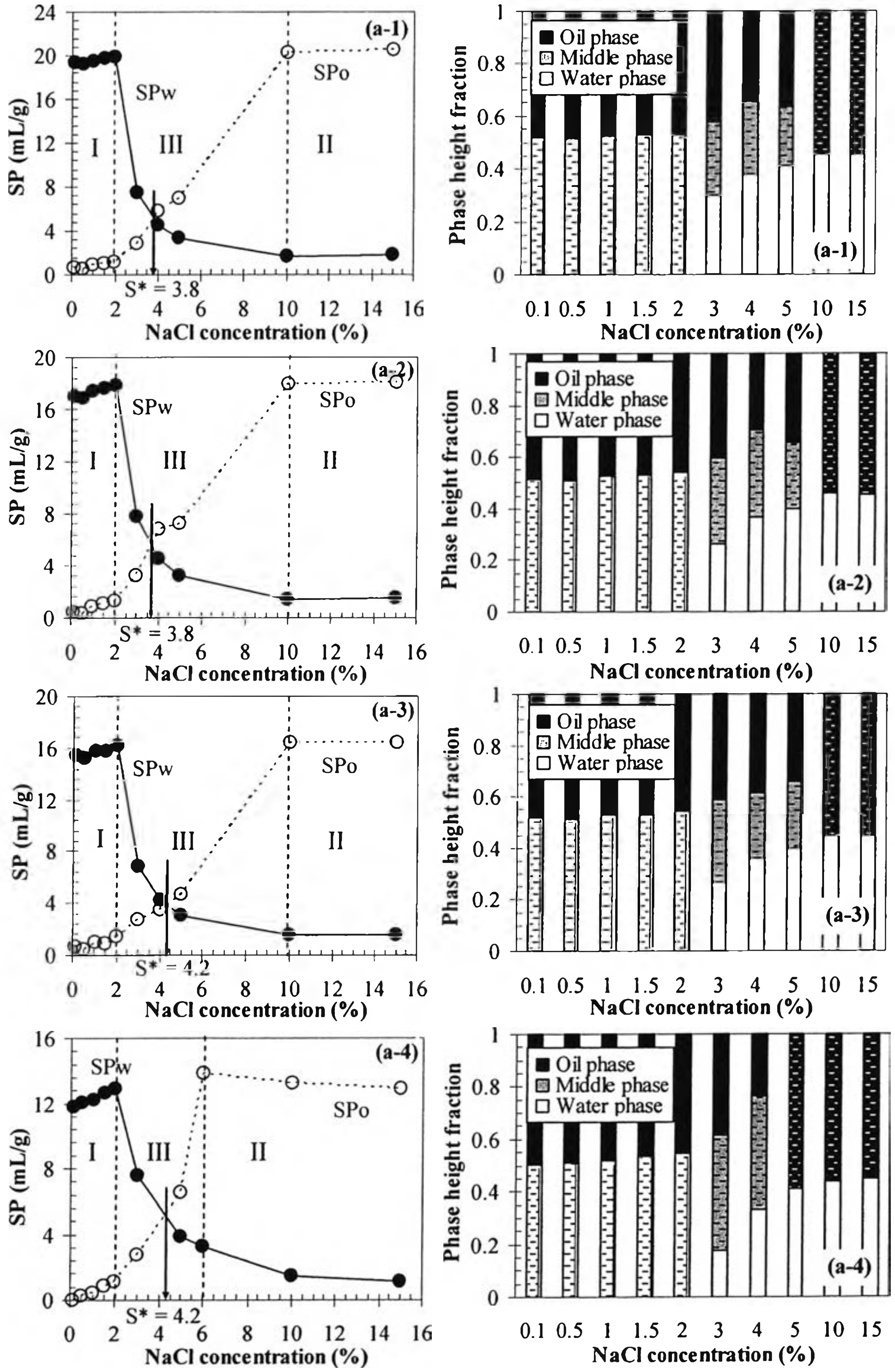


Figure 6.1 Solubilization parameters (SP) and phase height fraction as a function of NaCl concentration and $C_{14-15}(PO)_3SO_4Na$ concentration at an initial oil-to-water volumetric ratio of 1 to 1 and 5% $C_{12-14}H_{25-29}O(EO)_5H$ and: (a-1) 0.1% $C_{14-15}(PO)_3SO_4Na$, (a-2) 0.3% $C_{14-15}(PO)_3SO_4Na$, (a-3) 0.5% $C_{14-15}(PO)_3SO_4Na$, and (a-4) 1% $C_{14-15}(PO)_3SO_4Na$.

The concentration of $C_{14\text{-}15}(PO)_3SO_4Na$ could not exceed 1% because at higher concentrations, the mixed surfactant solution became very turbid and is not appropriate for use as a liquid detergent formulation since the turbidity indicates the presence of multiple phases. The effects of $C_{14\text{-}15}(PO)_3SO_4Na$ and NaCl concentrations on solubilization parameters and the phase heights are illustrated in Figure 6.1. The crosshatch areas in the figure show the microemulsion phase or phase in which the surfactant is predominantly located for each type of microemulsion. As expected, an increase in salinity results in a phase shift from Winsor Type I to Winsor Type III and to Winsor Type II microemulsions for any given $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ concentration. Interestingly, it was clearly seen that using only 0.1% $C_{14\text{-}15}(PO)_3SO_4Na$, the solution was composed of a large fraction the middle phase microemulsion in the NaCl concentration range of 3 to 5%. The volume of the middle phase significantly increases with increasing $C_{14\text{-}15}(PO)_3SO_4Na$ concentration, and the optimum salinity (S*) slightly increases. A concentration of 0.1% $C_{14\text{-}15}(PO)_3SO_4Na$ was selected for further investigation because this low concentration of $C_{14\text{-}15}(PO)_3SO_4Na$ still provides a relatively large volume fraction of the middle phase, or Winsor Type III microemulsion.

Next, the effect of $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ concentration on microemulsion formation was studied by varying the concentration of $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ from 3 to 8% at a constant $C_{14\text{-}15}(PO)_3SO_4Na$ concentration of 0.1%. Figure 6.2 shows the SP parameters and phase height as a function of $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ and NaCl concentrations. The concentration of $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ was started at 3% because the middle phase microemulsion first appears at this concentration. The volume fraction of the middle phase increased with increasing $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ concentration at the optimum salinity. In the studied range of $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ concentration, 5% $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ was selected for further investigation since it corresponds to a reasonably high solubilization and a large portion of middle phase microemulsion. The present formulation with only two surfactants can form the middle phase microemulsion, while three surfactants were needed in the previous formulations [14-17]. This might be explained by the fact that the structure of $C_{14\text{-}15}(PO)_3SO_4Na$ contains the PO group, which can improve the hydrophobicity, and $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ is an excellent oil soluble emulsifier. From the results, a mixture of 0.1% $C_{14\text{-}15}(PO)_3SO_4Na$ and 5% $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ was used as the selected formulation for subsequent phase diagram studied and IFT measurements to investigate the effects of water hardness.

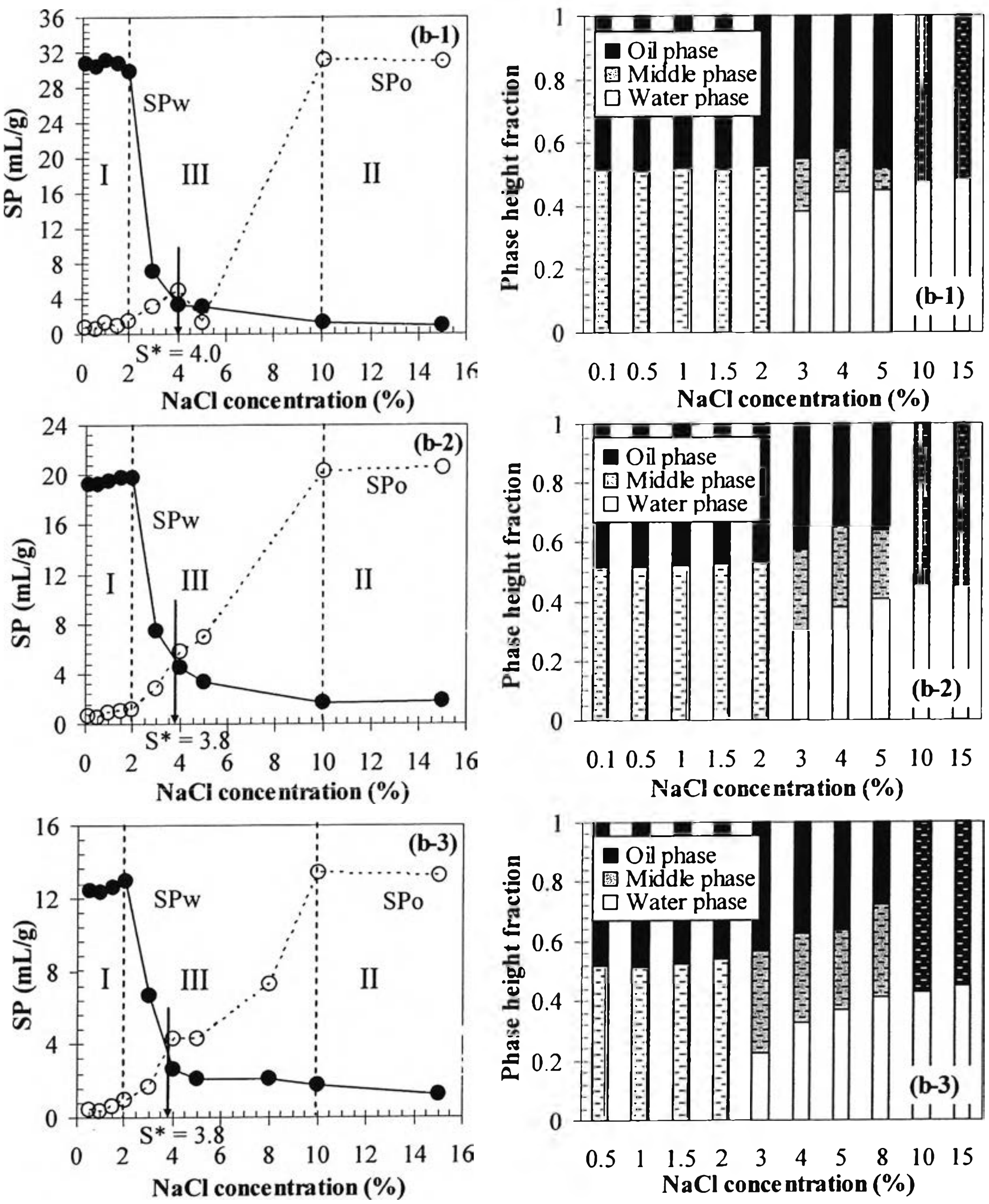


Figure 6.2 Solubilization parameters (SP) and phase height fraction as a function of NaCl concentration and $C_{14\text{-}15}(PO)_3SO_4Na$ concentration at an initial oil-to-water volumetric ratio of 1 to 1 and 0.1% $C_{14\text{-}15}(PO)_3SO_4Na$ and: (b-1) 3% $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$, (b-2) 5% $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$, and (b-3) 8% $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$.

6.4.2 Effect of Water Hardness on Microemulsion Formation and IFT

In order to observe the effect of water hardness on the SP of different microemulsion systems, both $C_{14\text{-}15}(PO)_3SO_4Na$ and $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ concentrations were fixed at 0.1% and 5%, respectively, and water hardness was varied from 0 to 1000 ppm. As can be seen in Figure 6.3, with increasing water hardness, the optimum salinity (S*) tends to slightly decrease but the optimum SP remains almost unchanged.

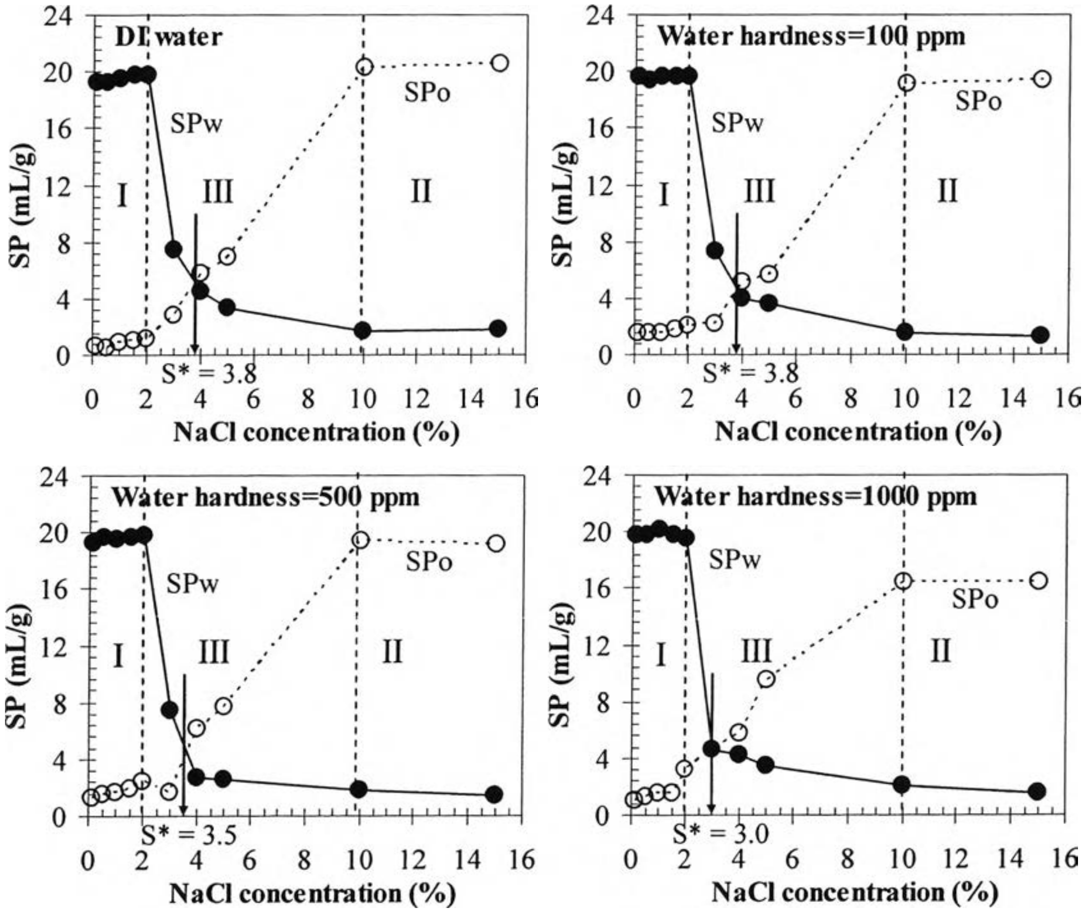


Figure 6.3 Solubilization parameters (SP) as a function of NaCl concentration and water hardness at an initial oil-to-water volumetric ratio of 1 to 1 with 5% $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ and 0.1% $C_{14\text{-}15}(PO)_3SO_4Na$.

The equilibrium IFT as a function of salnity in Figure 6.4 was measured between an aqueous solution of the selected formulation and the dyed motor oil in order to simulate a system close to that the actual situation in the wash step. The total surfactant concentration was kept constant at 0.3% (based on result in Figure 6.8), which was prepared from diluting a solution of the selected formulation composed of 0.1% $C_{14-15}(PO)_3SO_4Na$ and 5% $C_{12-14}H_{25-29}O(EO)_5H$ or 2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$. As seen in Figure 6.4, for any given salinity, the equilibrium IFT increases with increasing water hardness. As seen in Figures. 6.3 and 6.4, the optimum salinity is approximately 4% NaCl at all water hardness levels studied and does not vary systematically with water hardness.

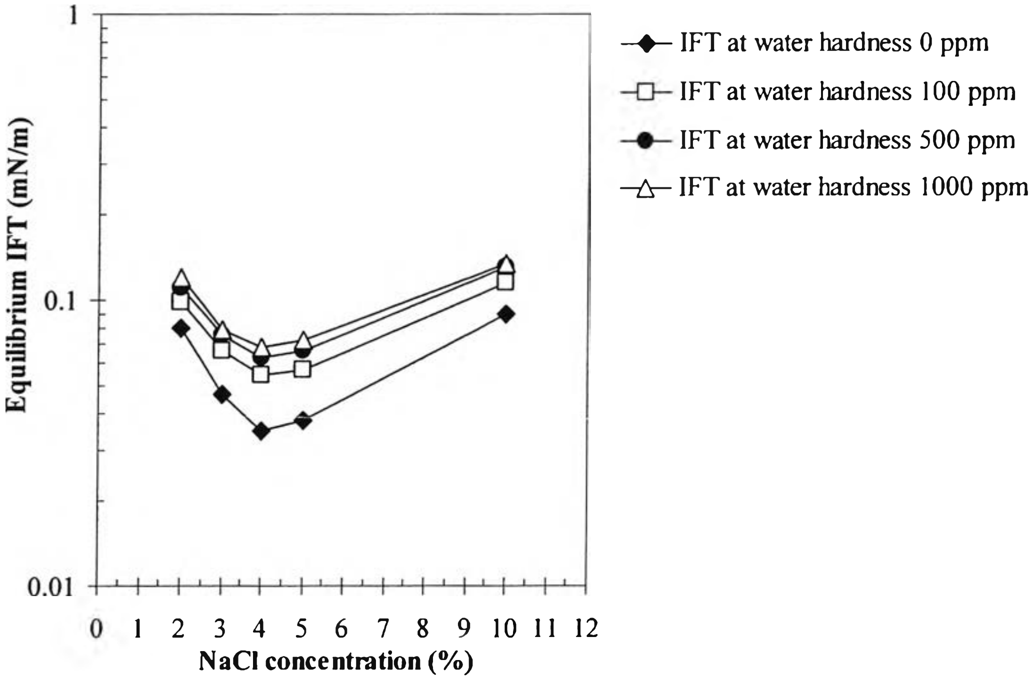


Figure 6.4 Euilibrium IFT between the dyed motor oil and the aqueous solution of the selected formulation (2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$) at different NaCl concentrations and water hardness levels.

When phase boundaries between Winsor Type I, II, III, and IV microemulsions are shown on surfactant concentration vs salinity (or vice versa), these plots are known as fish diagrams [31-36]. 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 a 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 [32]. If a studied system consists of oil, water, and a nonionic surfactant, the role of salt or cosurfactant is replaced by temperature [34,35].

The Type III to IV transition occurs at surfactant concentrations far higher than those used in detergency applications and so was not investigated here. 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 6.5 illustrates the IFT of an equilibrium system and a dynamic system as a function of total surfactant concentration of the selected formulation (a diluted samples of 0.1% $C_{14-15}(PO)_3SO_4Na$ and 5% $C_{12-14}H_{25-29}O(EO)_5H$ or 2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$ of the total actives) at 4% NaCl. The equilibrium microemulsion system was obtained after one month of phase equilibration while for dynamic measurements, the phases of the studied microemulsion system were taken at 20 min. Typically, there are two surfactant concentrations at which there is a sharp decrease in the IFT with increasing surfactant concentration: the first concentration is the CMC where micelle begins to form in aqueous phase: the second concentration is the CμC where the Winsor Type I transitions to the Type III microemulsion [37]. From Figure 6.5, the CMC and CμC were found at 0.015% and 0.06% of total surfactant concentration, respectively. The CMC value obtained from Figure 6.5 is also confirmed by the CMC value determined from the plot between surface tension and total surfactant concentration, as shown in Figure 6.6, the traditional method of determining the CMC [38]. Equilibration time does not affect the CMC or the CμC, as shown in Figure 6.5 for equilibrium vs dynamic IFT results so, the CμC obtained are relevant to the conditions used in our washing experiments, where 20 min washing time was used.

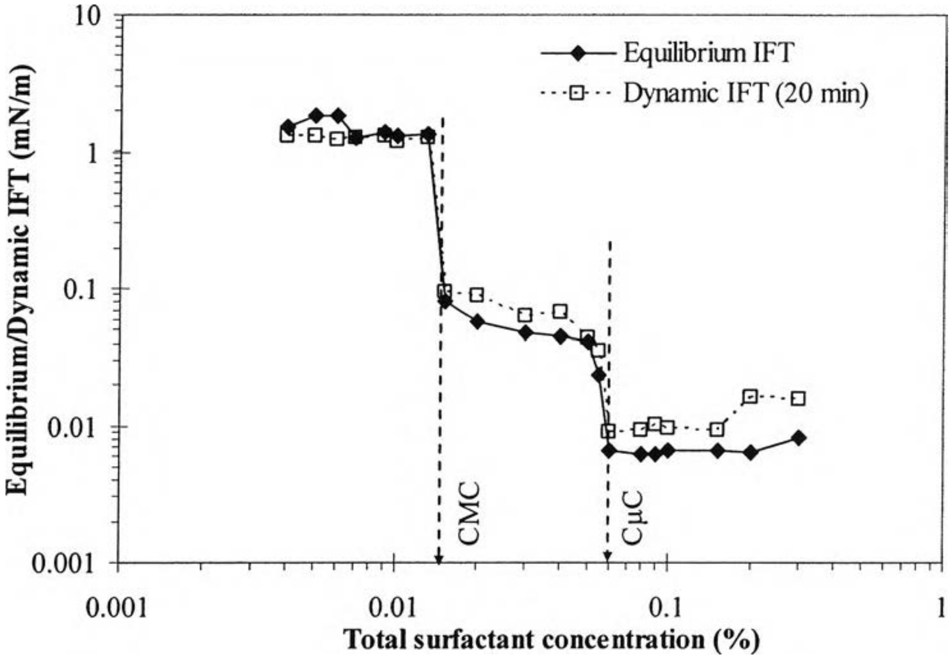


Figure 6.5 Equilibrium and dynamic IFT at 20 min as a function of total surfactant concentration at 30 °C using the selected formulation (0.1% $C_{14-15}(PO)_3SO_4Na$ and 5% $C_{12-14}H_{25-29}O(EO)_5H$, or 2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$) with 4% salinity.

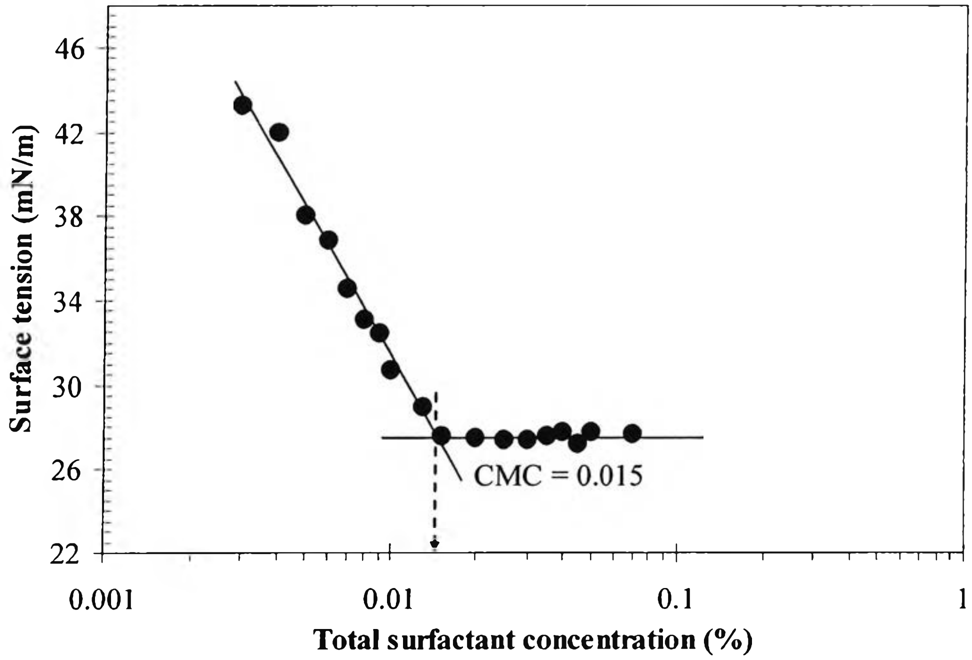


Figure 6.6 Surface tension of the mixed surfactant system with 4% salinity for the motor oil system.

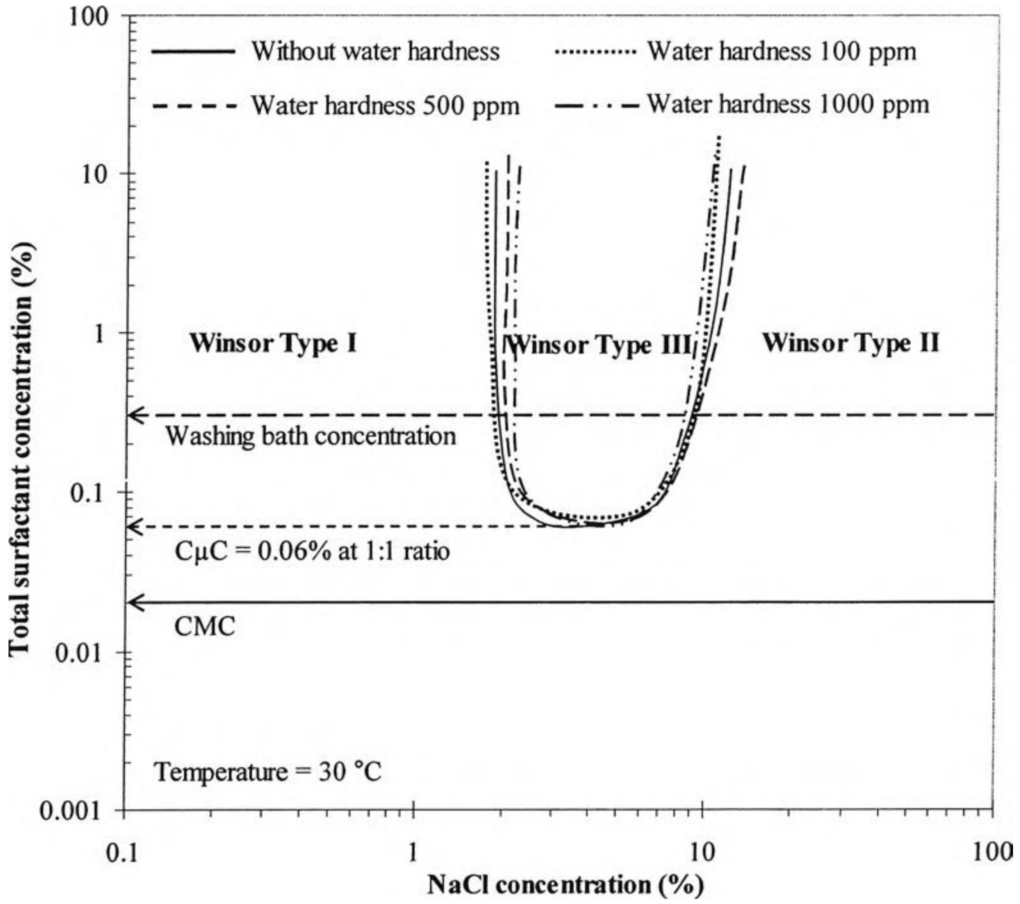


Figure 6.7 Fish phase diagram of the selected formulation (2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$) at an oil-to-water volumetric ratio of 1 to 1 at different degrees of water hardness.

Figure 6.7 illustrates the fish diagram for our selected surfactant mixture as a function of water hardness at a 1:1 oil-to-surfactant solution volumetric ratio and at 30 °C. In the studied range of water hardness, water hardness did not affect the fish diagram, due to the very small level of anionic surfactant in the mixture (2 parts $C_{14-15}(PO)_3SO_4Na$ in the formulation). In addition, the effect of adding builder in the presence of water hardness on microemulsion formation at 1:1 oil-to-water volumetric ratio was also observed at 1000 ppm of water hardness and at 5:1 builder-to-water hardness mole ratio. With adding excess builder in the system, the phase transformation of microemulsion type as varying salinity was coincide with the system in the presence of 1000 ppm of water hardness without adding builder. For any given degree of water hardness, the CμC was found at a very low surfactant concentration of about 0.06%. From the fish diagram, the selected formulation could produce a Winsor Type III microemulsion in the salinity range of 2 to 10%. The total surfactant concentration of 0.3% in the washing bath used for the detergency experiments, which will be discussed later, is located in the Winsor Type III region, which is slightly higher than the CμC (0.07%) and much higher than the CMC (0.015%). Therefore, it can be noted that the washing bath used in the detergency experiments can still provide the middle phase microemulsion condition, which often corresponds to high detergency performance [15,16].

6.4.3 Effect of Total Surfactant Concentration on Detergency Performance

Figure 6.8 shows oil removal as a function of the total surfactant concentration of the washing solution. The different concentrations of the selected formulation were prepared from diluting a solution of the selected formulation composed of 0.1% $C_{14-15}(PO)_3SO_4Na$ and 5% $C_{12-14}H_{25-29}O(EO)_5H$ or 2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$. In addition, the commercial detergent was diluted from 14.5% total surfactant concentration to different concentrations for comparison with the selected formulation. The approximate surfactant compositions supplied by the commercial detergent manufacturer were used to estimate surfactant concentrations. The selected formulation gave a much higher detergency performance than the commercial detergent at any given total surfactant concentration. For the selected formulation, detergency performance steadily increased with surfactant concentration and it plateaued at 79-84% above about 0.1% surfactant concentration. Hence, a 0.3% surfactant concentration of the selected formulation (2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$) was considered as the optimum concentration for laundering. The appearance of the fabric before and after the washing process by using 0.3% total surfactant concentration of the selected formulation is shown in Figure 6.9. The brightness of the fabric after washing appeared nearly the same as before soiling the fabric with dyed oil consistent with the 84% oil removal. Table 6.1 gives a comparison of motor oil detergency performance of the present study with our previous studies; the present formulation provides a slightly higher oil removal than those previous formulations [14-17].

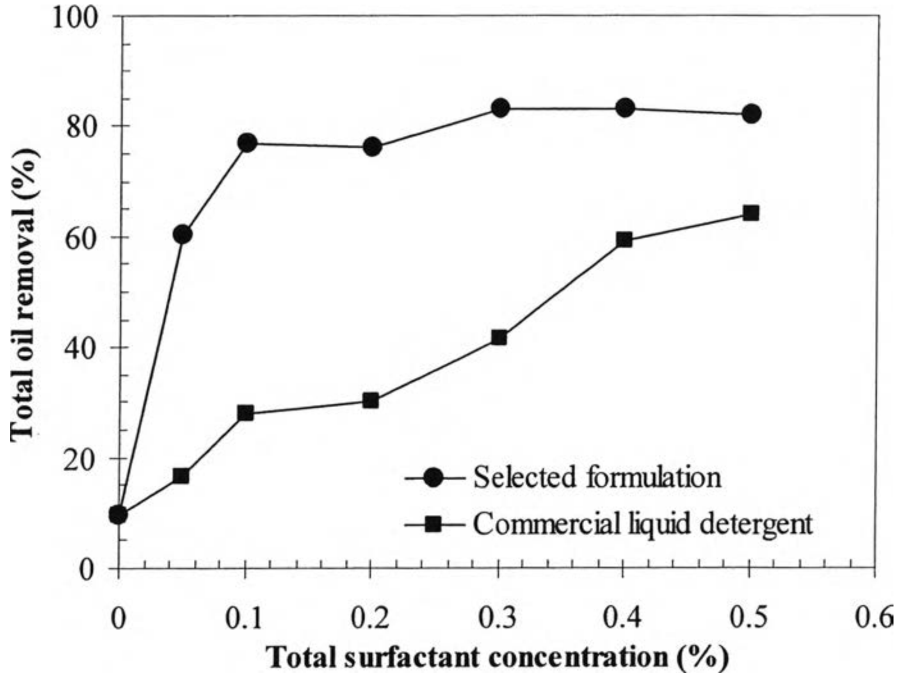
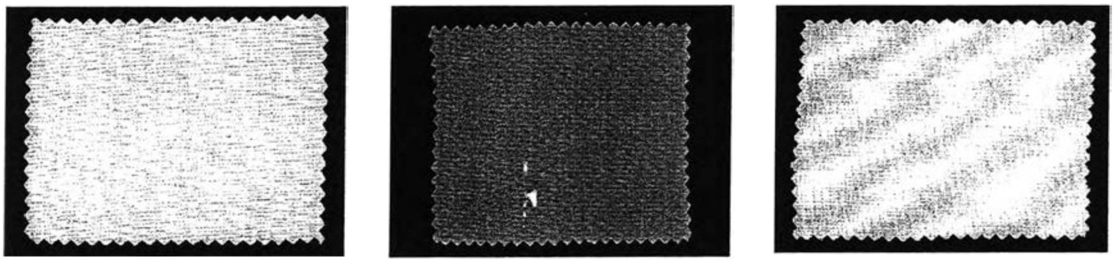


Figure 6.8 Effect of total surfactant concentration on oil removal of the selected formulation (2 parts $C_{14\text{-}15}(PO)_3SO_4Na$ and 98 parts $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$) at 4% of salinity and 30 °C.



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

Figure 6.9 Standard photographs of: (a) unsoiled fabric, (b) soiled fabric with dyed motor oil, and (c) fabric after washing with 0.3% total surfactant concentration of the selected formulation (2 parts $C_{14\text{-}15}(PO)_3SO_4Na$ and 98 parts $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$) with the 4% salinity.

Table 6.1 The detergency performance of motor oil removal compared to previous studies [14-17].

Comparison	Tongcumpou *et al.* [14-16]	Tanthakit *et al.* [17]	The present work
Surfactant composition in the formulation	28.6 parts ADPODS 42.9 parts AOT 28.6 parts Span 80	13 parts ADPODS 43.5 parts AOT 43.5 parts Span 80	2 parts $C_{14-15}(PO)_3SO_4Na$ 98 parts $C_{12-14}H_{25-29}O(EO)_5H$
Total surfactant concentration in the formulation (%)	7	11.5	5.1
Total surfactant concentration in the washing bath (%)	0.112	0.115	0.3
NaCl concentration in washing bath (%)	16	2.83	4
Washing temperature (°C)	30°C	30°C	30°C
Maximum oil removal (%)	78	83	84
Detergents regulation	ADPODS can be used in I&I *(applications until Oct 2007)		Passed

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

6.4.4 Effect of Water Hardness and Builder on Detergency Performance

The washing experiments were carried out at different water hardness levels with the standard polyester/cotton blend as a testing fabric. In the detergency experiments, the same degree of water hardness was added in the rinsing water as that in the washing solution. Again, a 0.3% total surfactant concentration used for the detergency experiments was prepared from diluting the selected formulation (2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$). Figure 6.10 shows the total oil removal and the IFT between the aqueous surfactant solution and the dyed oil as a function of water hardness at 4% salinity (IFT datum from Figure 6.4).

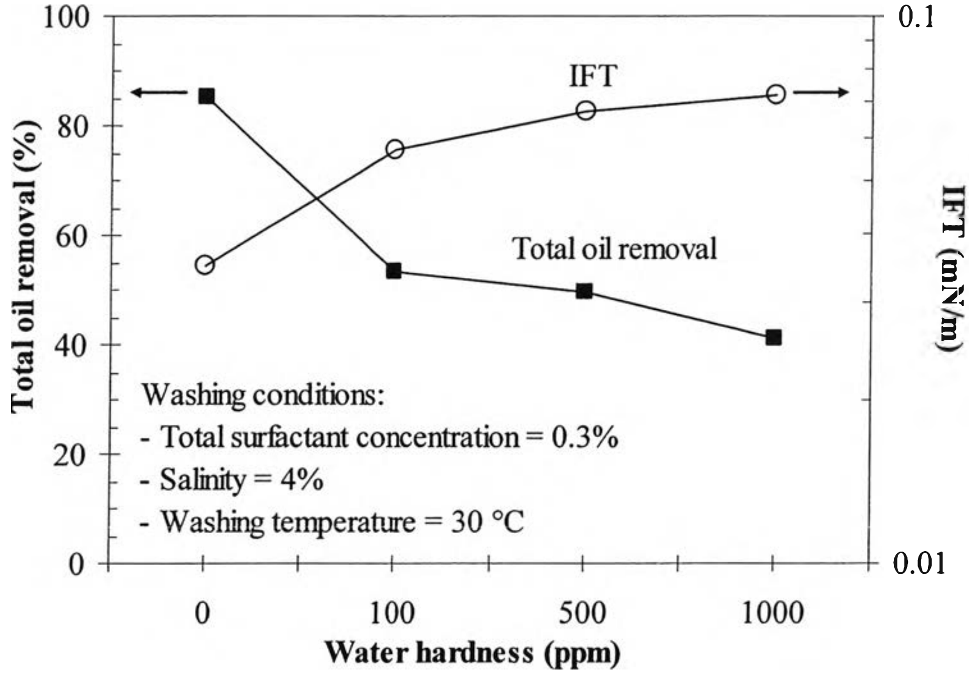


Figure 6.10 The total oil removal and the equilibrium IFT between oil and washing solution of the selected formulation at 4% salinity with different degrees of water hardness using a polyester/cotton blend at 30 °C.

As the water hardness increased, the total oil removal tended to decrease significantly, whereas the IFT only slightly increased. These results can be hypothesized that the divalent cations of water hardness coadsorb on the fabric with the surfactant (divalent cations acting as a bridge between negatively charged surfactant and the negatively charged sites on the fabric). The calcium ions (divalent cation) and anionic surfactant synergistic coadsorption was found in the studying behavior for soap (octanoate) adsorption on carbon black with calcium [38]. Therefore, low surfactant avialable in the washing solution leads to a lowering of surfactant molecules adsorbing on the interfacial surface between the washing solution and the stained oil, resulting in increasing of IFT and a lowering of oil removal. Interestingly, the main composition of the selected formulation was $C_{12-14}H_{25-29}O(EO)_5H$, a nonionic surfactant, which might be difficult to coadsorb with divalent cations. However, it was found that calcium ion can interact with the lonepair electrons in the oxygen atom of the ether radical in polyoxyethylenes as a coordinating agent in nonionic surfactants (alcohol ethoxylate) in the presence of water hardness [39]. Therefore, the nonionic surfactant present in the selected formulation possibly interacts partially with the divalent cations, resulting in a lowering of nonionic surfactant molecules for laundering.

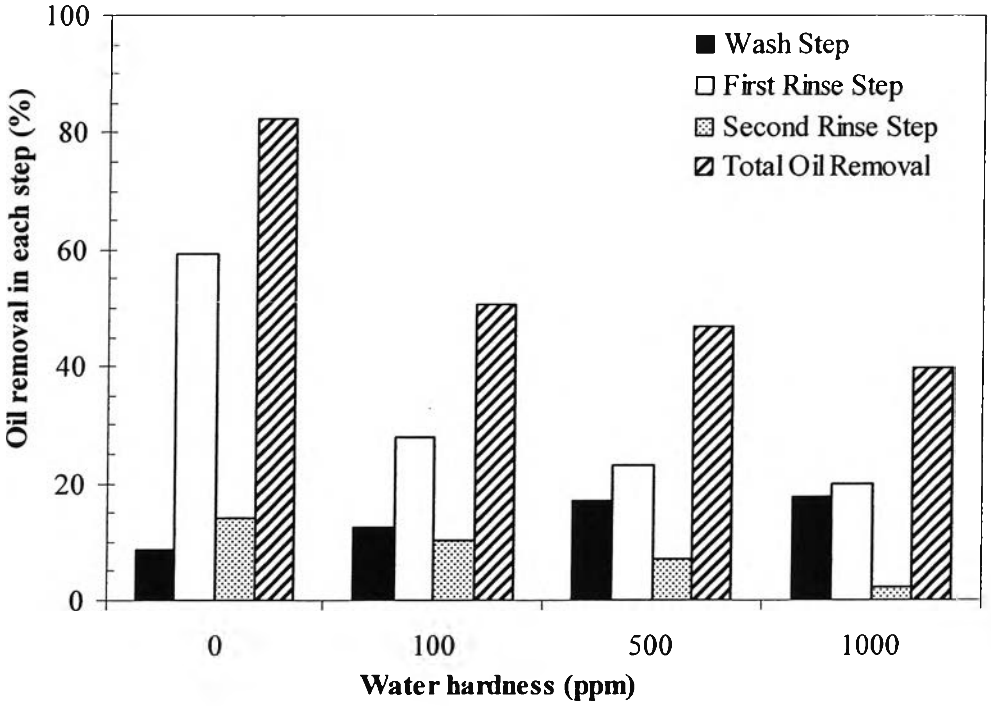


Figure 6.11 The total oil removal and the equilibrium IFT between oil and washing solution of the selected formulation at 4% salinity with different degrees of water hardness using a polyester/cotton blend at 30 °C.

The percent oil removal at each step and the total oil removal from the polyester/cotton blend fabric using a 0.3% total surfactant concentration of the selected formulation at 4% NaCl at different degrees of water hardness are shown in Figure 6.11. As the water hardness increased, the oil removal in the wash step increased slightly while the oil removal in the first and second rinse steps decreased remarkedly. In the case of washing without water hardness, the oil removal in the first rinse step was found to be much higher than that in the wash step. This is due to the lowest IFT at 0 ppm water hardness, as indicated in Figure 6.10, causing more oil penetration into the fabric structure, known as the spreading effect [15,16]. As a result, the oil removal was very low in the wash step but very high in the first rinse step [16]. The total oil removal decreased with increasing water hardness. From the results, the efficiency of oily soil removal is believed to relate to the adsorption of both the surfactants and the divalent cations on the surface of the fabric as well as the intereaction between the divalent cations and the surfactants.

To observe the effect of adding a builder, the total surfactant concentration in the washing solution was still fixed at 0.3% and both washing and rinsing solutions had a constant water hardness of either 0 or 500 ppm while the concentration of each builder (STPP or EDTA) was varied. Each studied builder was added only in the washing solution. Figure 6.12 illustrates the total oil removal as a function of builder concentration using the polyester/cotton blend as the testing fabric under the absence of water hardness. Insignificant differences in the total oil removal were found with increasing builder concentration, suggesting that adding builders to the system without water hardness does not affect the detergency performance. In addition, the effect of builder-to-water hardness ratio on the total oil removal is shown in Figure 6.13. The washing results, under the presence of both water hardness and builder, showed that the addition of builder enhanced the detergency performance only at a certain level. The results can be explained in that a builder can bond with the divalent cations. These results also suggest that some divalent cations still be the coordinating agent and coadsorption, even at high builder-to-water hardness ratios. In a comparison between the two studied builders, STPP was found to be slightly better than the EDTA.

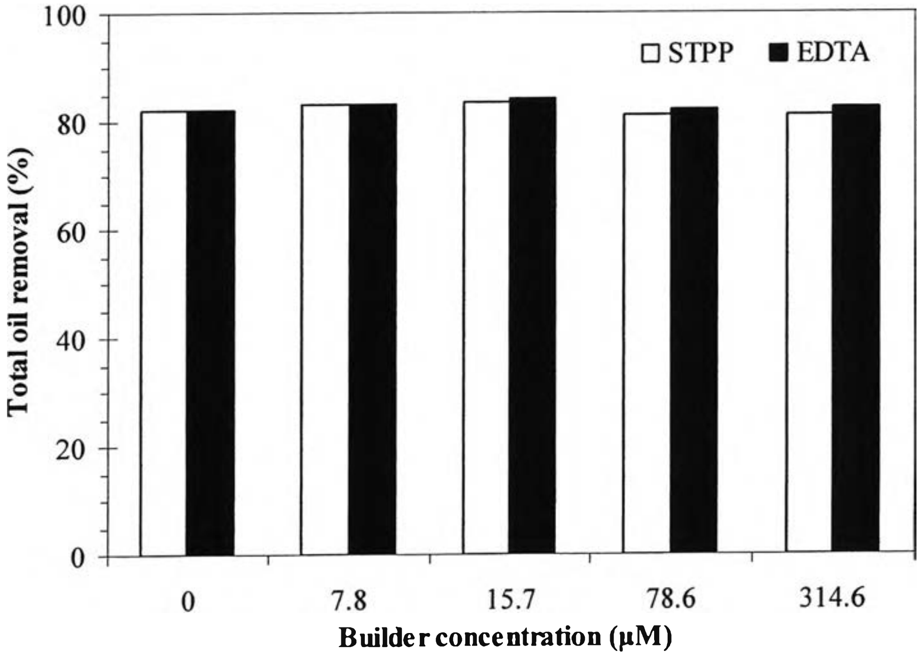


Figure 6.12 Total oil removal at different builder concentrations using 0.3% total surfactant concentration of the selected formulation without adding water hardness at 30 °C.

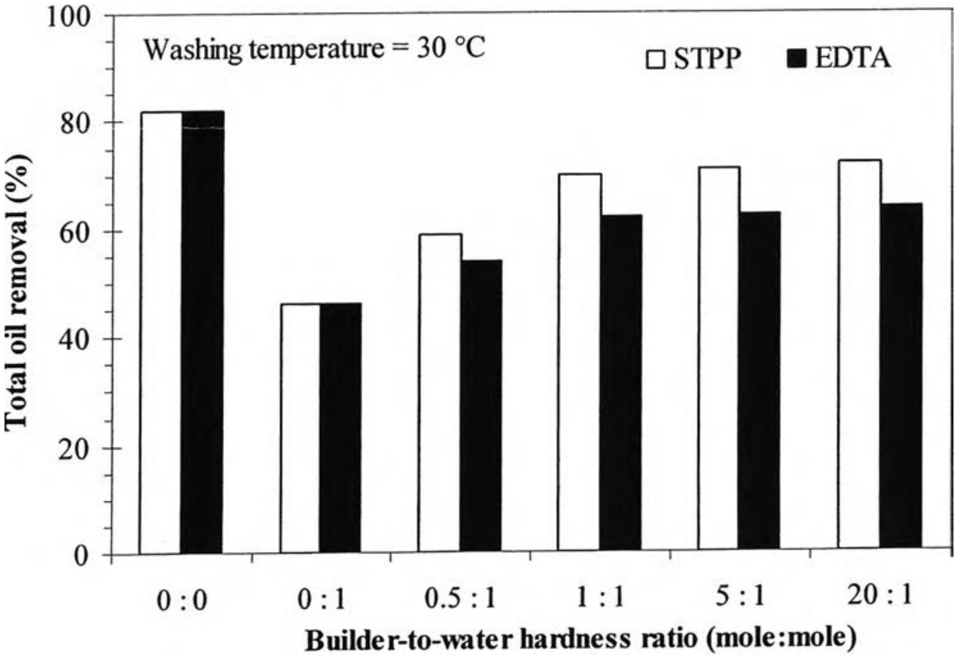


Figure 6.13 Total oil removal at different builder-to-water hardness molar ratios using a 0.3% total surfactant concentration, prepared from the selected formulation and 500 ppm water hardness in both washing solution and rinsing water.

6.4.5 Effect of Builder on Free Divalent Cation Concentration

In order to study the effect of a builder on the amount of free divalent cations remaining in solution, water hardness in solution was kept constant at 500 ppm with different STPP concentrations in the washing solution with and without the polyester/cotton blend fabric. Figure 6.14 shows the amount of free divalent cations remaining in the solution after the wash step with and without the testing fabric as a function of builder-to-water hardness molar ratio in the absence of surfactants. The free divalent cations decreased with increasing builder-to-water hardness molar ratio. In addition, it was found that the amount of free divalent cations was almost zero at a builder-to-water molar hardness ratio greater than 1 to 1. Hence, under the surfactant-free condition, the use of a builder with equal or excess amounts can bond all divalent cations in the solution. For any given builder-to-water hardness molar ratio less than one-to-one molar ratio, there was a lower amount of free divalent cations with the testing fabric than without the fabric, suggesting that the divalent cations can adsorb on the fabric surface.

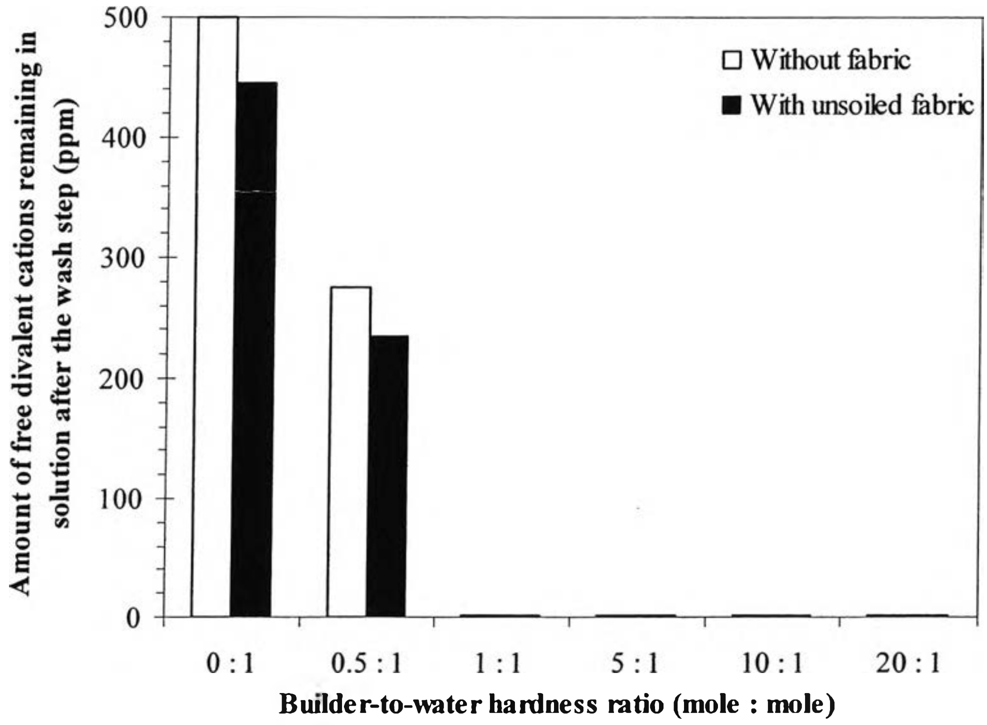


Figure 6.14 Amount of free divalent cations remaining in solution at different builder-to-water hardness molar ratios with and without the polyester/cotton blend fabric, in the absence of surfactants.

Figure 6.15 shows the effect of builder-to-water hardness molar ratio on the amount of free divalent cations remaining in the solution after the wash step using a 0.3% washing solution prepared from the selected formulation at 4% salinity. The results showed that the free divalent cations decreased with increasing builder-to-water hardness molar ratio and reached zero at the builder-to-water hardness molar ratio of 1 to 1 and higher. Interestingly, when surfactant molecules are present, the amount of free divalent cations was lower than that in the system using pure water as the washing solution (see Figures 6.14 and 6.15). The results suggest that the divalent cations can still patially coadsorp between surfactant molecules and fabric, even when there is a builder. However, adding a builder in the system with hard water was found to effectively improve the oil detergency performance at a certain level (see Figure 6.13).

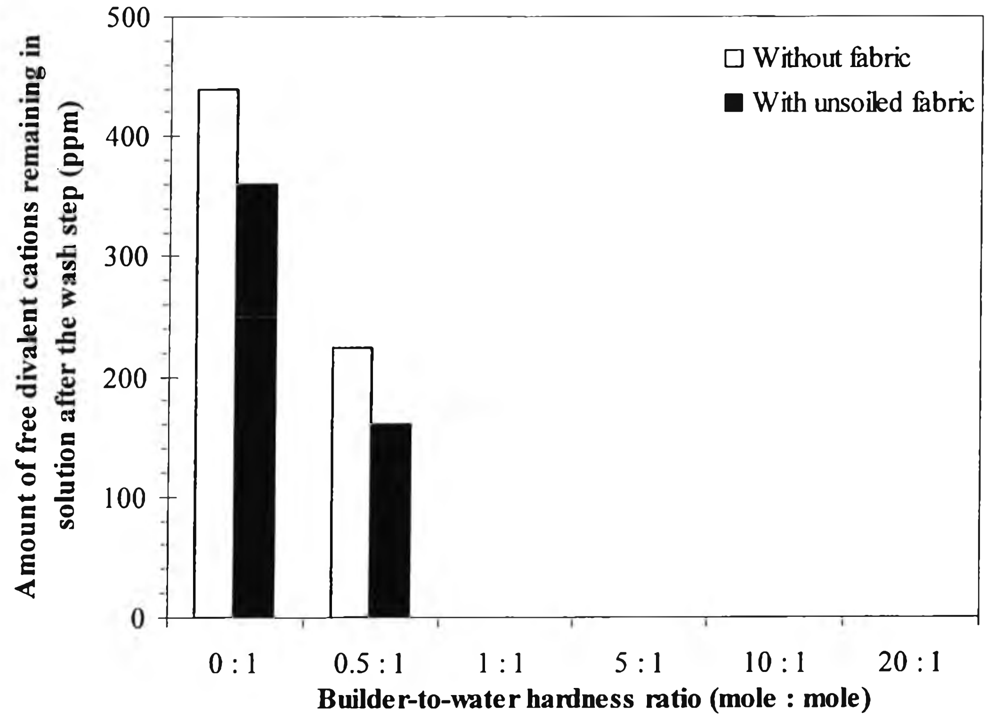


Figure 6.15 Amount of free divalent cations remaining in solution at different builder-to-water hardness molar ratios with and without the polyester/cotton blend fabric using a washing solution containing 0.3% total surfactant concentration prepared from the selected formulation.

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6.6 References

1. 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
2. Whang HS, Kim YJ, Ko SW (2001) Effect of Hydrophile-Lipophile Balance Values of Surfactant Mixtures on the Detergency of Oily-Soiled Single Fiber. Text Res J 71:650-654
3. 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
4. Doshida SG, Saito M, Nagayama M (2003) Effects of Calcium Present in Fabric and the Washing Liquor on Detergency. J Oleo Sci 52:73-82
5. McDonell JA, Liu A (1987) An Improved Method for Evaluating Detergent Builders for Water Hardness Control. J Am Oil Chem Soc 64: 769-776
6. Nagarajan MK, Paine HL (1984) Water Hardness Control by Detergent Builders. J Am Oil Chem Soc 61:1475-1478

7. Cohen L, Moreno A, Berna JL (1993) Influence of Calcium Concentration in the Washing Liquor on Detergency Performance of Linear Alkylbenzene Sulfonate. J Am Oil Chem Soc 70:79-82
8. Matheson KL, Cox MF, Smith DL (1985) Interactions between Linear Alkylbenzene Sulfonates and Water Hardness Ions. I Effect of Calcium Ion on Surfactant Solubility and Implications for Detergency Performance. J Am Oil Chem Soc 62:1391-1396
9. National Ground Water Association (accessed Aug. 2008) Dissolve Mineral Sources and Significance. http://www.ngwa.org/public/gwtools/dissolved_minerals.aspx
10. Heidekamp AJ, Lemley AT (2005) Hard Water. Water Bulletin. Water Quality Program, College of Human Ecology, Cornell University (April, 2005)
11. Water Quality and Waste Management of North Carolina Coorperative Extension Service (accessed Aug. 2008) Water Quality and Laundry Problems. http://www.bae.ncsu.edu/programs/extension/publicat/wqwm/tc1.html
12. Rosen MJ (2004) Surfactants and Interfacial Phenomena (3rd edition), Wiley, New York, pp 362-363
13. Sachdev A, Krishnan S (1997) Heavy-Duty Liquid Detergents. In: Lai KY (ed) Liquid Detergents (Surfactant Science Series Vol. 67). Marcel Dekker, New York, pp 261-318
14. 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 Surfact Deterg 6:191-203
15. 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 Surfact Deterg 6:205-213
16. Tongcumpou C, Acosta EJ, Quencer LB, Joseph AF, Scamehorn JF, Sabatini DA, Yanumet N, Chavadej S (2005) Microemulsion Formation and Detergency of Oily Soils: III Performance and Mechanisms. J Surfact Deterg 8:147-156

17. Tanthakit P, Chavadej S, Scamehorn JF, Sabatini DA, Tongcumpou C (2008) Microemulsion Formation and Detergency with Oily Soil: IV Effect of Rinse Cycle Design. J Surfactants Deterg J Surfact Deterg 11:117-128
18. 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
19. Bidyut KP, Satya PM (2001) Uses and Applications of Microemulsions. Curr Sci India 80:990-1001
20. Dörfler HD, Grosse A, Krüssmann H (1996) The Use of Microemulsions as Cleaning Media. Tenside Surfact Deterg 33:432-440
21. 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
22. 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
23. Broze G (1994) Mechanisms of Soil Removal. In: Lange KR (ed) Detergents and Cleaners: A Handbook for Formulators. Hanser, Munich, pp 29-41
24. 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 Disp Sci Technol 4:313-329
25. 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 Disp Sci Technol 7:331-343
26. 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.
27. Scamehorn JF, Sabatini DA, Harwell JH (2004) Surfactants, Part I: Fundamentals In: Atwood JL, Steed JW (eds) Encyclopedia of Supramolecular Chemistry. Marcel Dekker, New York, pp 1458-1469
28. Standard Guide for Evaluating Stain removal Performance in Home Laundering (2000) Annual Book of ASTM Standards, vol 15.04. American Society for Test and Materials ASTM D 4265-98, West Conshohocken

29. 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 Surfact Deterg 1:221-226
30. Standard Methods for the Examination of Water and Wastewater (1992) 18th edition, American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC, 2340C.
31. Salager JL (2000) Formulation Concepts for the Emulsion Maker. In: Nielloud F, Marti-Mestres G (eds) Pharmaceutical Emulsions and Suspensions. Marcel Dekker, New York, pp 19-72
32. Kegel WK, Lekkerkerker HNW (1993) Competition between a Lamellar and a Microemulsion Phase in an Ionic Surfactant System. J Phys Chem 97:11124-11133
33. Bastogne F, David C (1998) Quaternary N-alkylaldonamide-Brine-Decane-Alcohol System Part I: Phase Behaviour and Microemulsions. Colloids Surf A Physicochem Eng Asp 139:311-320
34. Lee JM, Lim KH (2004) Changes in Morphology of Three-Phase Emulsions with Temperature in Ternary Amphiphile/Oil/Water Systems. Colloids Surf A Physicochem Eng Asp 248:57-65
35. Lee JM, Lim KH (2005) Changes in Two-Phase Emulsion Morphology in Temperature-Amphiphile Concentration or Fish Diagram for Ternary Amphiphile/Oil/Water Systems. J Colloid Interface Sci 290:241-249
36. 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
37. Acosta EJ, Harwell JH, Sabatini DA (2004) Self-Assembly in Linker Modified Microemulsions. J Colloid Interface Sci 274:652-664
38. Technical Association of the Pulp and Paper Industry (TAPPI) (accessed Aug. 2008) Mechanisms of Collector Chemistry in Flotation Deinking: Parts I, II, and III. http://www.tappi.org/s_tappi/sec_publications.asp?CID=4865&DID=524836

39. Goto-Doshida S, Nagayama M (2003) Distribution of Calcium Ion in Wash System and Detergency: Calcium Ion Interaction with Surfactants, Builders and Cotton Fabrics. J Oleo Sci 52:317-329