

CHAPTER V
ENHANCING TRIOLIEN REMOVAL FROM FABRIC BY
MICROEMULSION FORMATION OF MIXED SURFACTANT SYSTEM

ABSTRACT: Microemulsion-based formulation approach was found successfully for detergency application with highly hydrophobic oils of hexadecane and motor oil in our previous work. The same approach was introduced to use with triolien, which is one of the most difficult oils to be removed from fabric. The linker concept was applied in this work for surfactant selection for microemulsion formation. The selected formulation consisted of three types of surfactant. Dihexyl sulfosuccinate or Aerosol - MA (AMA) was an ionic surfactant with a moderate hydrophile-lipophile balance (HLB), while secondary alcohol ethoxylate (Tergital15-S-5) and alkyl diphenyl oxide disulfonate (ADPODS) were used as lipophilic and hydrophilic surfactants, respectively. The formulations of these three surfactant mixtures with different ADPODS concentrations were studied. The phase behavior of each system as well as interfacial tension was determined. Then the studied formations from the phase study were selected for detergency experiment. The studied formulations at different salinities were conducted as a detergent to remove triolien on polyester/cotton sample fabric. The results showed the two peaks of maximum detergency in the range of salinity from 0.1% to 10% NaCl. The higher hydrophilic of the system, the higher salinity was required for the maximum detergency. The result of the dynamic interfacial tension and the detergency result from different rinsing method indicated that the second maximum detergency found at higher salinities was related to spreading effect and low interfacial tension. The first peak of maximum detergency is believed to be related to a phase separation of the washing solution.

KEY WORDS: Microemulsion, dihexyl sulfosuccinate, alkyl diphenyl oxide disulfonate, secondary alcohol ethoxylate, triolien, detergency

INTRODUCTION

Oily soil washing has been an important subject of interest in the area of detergency study for decades. Most natural oils are considered to be polar oils because of fatty acid or alcohol structures in their compositions. It is known that oily soils on fabric are not only simple hydrocarbon liquids but they can be polar and nonpolar oils, fatty acids, fatty alcohol and others. For the last few decades, a number of research works have been conducted using several types of oils in order to understand the mechanism of oil removal in detergency process.

Triolien or glycerol trioleate, a liquid form of triglycerides is a major component found in most natural fats from both plants and animals. It is present in many food products, such as cooking oil, margarine, butter, etc. Thus it considered to be a good representative as oily soil on clothes, and kitchenware for a detergency test. Studies on triolien removal by nonionic surfactants have been reported for decades (1). However, the phase behavior and the detergency mechanism for triolien have not yet well been understood.

Triolien has a molecular weight considerably higher than those of typical liquid hydrocarbons. For instance, a molecular weight of pure triolien is 885, compared to only 226 of a long chain hydrocarbon, hexadecane. In addition to its high molecular weight, it has a bulky structure of three branches to make it more difficult to be solubilized, even in common nonionic surfactants, linear alcohol ethoxylates (2). Figure 1 shows a molecular structure of triolien. Owing to fatty acid in its molecular structure, triolien is a slightly polar oil. The polar property of triolien makes its phase behavior so different from those of typical hydrocarbons. Alander and Warenheim (3,4) described the difference of the phase behaviors of long chain triglycerides and hydrocarbons in details with both the systems of nonionic and ionic surfactants. Their result showed that in the surfactant same system, replacing methyl ester with medium chain triglycerides or peanut oil affected both solubilization pattern and phase behavior significantly as a result of the large molecular size of triglycerides.

Most published papers on triolien removal involved nonionic surfactants since triolien is considerably highly hydrophobic and believed to be easier to be solubilized in a nonionic or a lipophilic surfactant than in a hydrophilic surfactant.

Triolien removal from a substrate was reported extensively by Dillan and co workers (1,5). They studied triolien removal from Polyester Mylar (thin polyester film) by using secondary alcohol ethoxylate with a hydrotrope (EDTA or Na_2CO_3). Their results showed that without hydrotrope, it was taken almost one and a half hours for triolien to be removed while in the system with EDTA, triolien was removed within 10 min. In addition, the paper explained the mechanism of the removal as complex formation and then necking or snap-off of the oil from the substrate occurred. Mori *et al.* (6) revealed their study on dynamic contact and detergency of triolien with a nonionic surfactant. The paper also related the phase behavior with detergency efficiency at different temperatures. Miller and coworkers extended their work on detergency by using a video microscope to observe the solubilization of oil droplet and its kinetics. They purposed that intermediate phase formation of liquid crystal was influenced detergency result (2,7,8,9). Thompson (10) investigated the major mechanism of oil removal from fabric for systems of nonionic, ionic and mixed surfactants. He argued that the maximum detergency did not always occur at the minimum interfacial tension.

From our previous study on phase behavior of mixed surfactants with motor oil and hexadecane (11), it was found that a mixture of a moderate HLB surfactant with the two cosurfactants which one is very highly hydrophobic and the other is highly hydrophilic exhibited a synergism to generate microemulsions with the two highly hydrophobic oils. This is because these two cosurfactants function similar to lipophilic and hydrophilic linkers; thus at the interface the two surfactants can facilitate the oil to be solubilized in microemulsion. This approach was also applied in this study with triolien. In the present study, mixtures of nonionic surfactant and two ionic surfactants were proposed as studied systems. Secondary alcohol ethoxylate was selected as it was found to work well with triolien (1,9). In addition, the two anionic surfactants of alkyl diphenyl oxide disulfonate (ADPODS) and dihexyl sulfosuccinate were used with the secondary alcohol ethoxylate to form microemulsion with triolien. From our preliminary experimental result, a mixture of these three surfactants was found to be able to form microemulsion with triolien. In addition, in the absence of ADPODS, microemulsion formation with triolien still existed but the system had a very low solubilization. In the present study, three

formulations of mixed surfactants were used to form microemulsion with salinity scan. For the phase behavior experiment, interfacial tension and water content were also measured. Furthermore, the detergency experiment using studied formulations was carried out. Then the correlation between the phase behavior of the studied systems and the detergency results was demonstrated as well as the mechanism of the oil removal was discussed

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials. Alkyl diphenyl oxide disulfonate (ADPODS) known as Dowfax 8390, ionic surfactant was supplied by Dow Chemical Co. Secondary alcohol ethoxylate known as Tergital 15-S-5 (TM5), a commercial grade nonionic was also supplied by Dow Chemical Co. (Midland, MI, USA). TM5 is a mixture of species with an alcohol group located at various positions along a chain of 12 to 15 carbon atoms with an average ethane oxide number of 5. Dihexyl sodium sulfosuccinate, a commercial grade ionic surfactant known as Aerosol-MA 80 or AMA was obtained from ICI Uniquema Co. (Wilmington, DE, USA). Properties and selected characteristics of the studied surfactants are shown in Table 1. The oil used in the experiment was triolien, practical grade (65%) purchased from Sigma (Milwaukee, WI).

Procedures. Phase studies were prepared by first mixing a surfactant solution in and triolien at the same volumetric ratio a flat bottom screw cap tube. The detail of the phase behavior experiment was described in our previous work (11). Interfacial tension (IFT) both of equilibrium and dynamic systems were measured by a spinning drop tensiometer (model 500, University of Texas, Austin, TX). The water contents in microemulsion phases were determined by Karl Fisher Coulometer. The preparation method of oily soil deposition on fabric was explained in our earlier work (12). The laundry experiment was conducted by using a Terg-O-Tometer (Model 7243 USA Testing Co. Inc. Hoboken, NJ) at 30 °C with 20 min wash cycle, 3 min first rinse and 2 min second rinse with deionized water.

Detergency performance was determined in terms of detergency efficiency (%D) from the change of reflectance of pre-washed and post-washed swatches; and % oil removal as prescribed in the previous study (12). Reflectance measurements

of the unsoiled swatches, the pre-wash soiled swatches and post-wash soiled swatches were conducted by using a colorimetric spectrophotometer (Hunter Lab, Ultra Scan Sphere model). Triolien concentration in the washing solution was determined by an extraction with dichloromethane and then measured the absorbance of the extracted solvent at 520 nm by a UV/VIS spectrophotometer (Hewlett Packard 8452 A).

In order to compare the effectiveness of the studied formulations, a commercial liquid detergent (CP) was used under the same laundering conditions. This commercial liquid detergent is a product of Procter & Gamble Co. (purchased in May 2002) under the trade name 'Tide', which is a leading commercial heavy-duty liquid laundry detergent in the US market. The percentage of total active surfactants in the commercial liquid detergent (CP) is estimated ca. to be 40% as a typical composition of liquid detergents (13).

RESULTS AND DISCUSSION

Phase behavior of the mixed surfactants with triolien. There were three formulations selected for the present study as shown in Table 2. They contained the three surfactants with different concentrations of ADPODS. The phase study of these three systems with salinity scan was performed at a water/oil ratio equal to one to one and at 30 °C. The plots between volume fraction and salt concentration of the systems of S1, S2 and S3 are shown in Figure 2. The graph shows that for the higher hydrophilicity corresponding to a higher ADPODS concentration, the higher salinity is required to form a middle phase and to obtain phase transition. This can be seen that the three systems S1, S2 and S3 exhibited the transition from 2 phases to 3 phases at 1.9, 2.4 and 3.0% NaCl, respectively. Unlike hydrocarbon oils, a system with triolien, especially with nonionic surfactants often exhibits other phases besides three Winsor's type microemulsions. Liquid crystal and sponge phases as sometimes referred in the literatures as L_{α} or LC and D' or L_3 , respectively are often found in the systems of nonionic surfactants with triolien (6,7,9,14,15). The formation of liquid crystal can be simply identified by using a polarized microscope to observe birefringence. All studied systems did not show birefringence indicating

that no liquid crystal phase formed. It can be explained by the fact that our studied systems contained high salinity which inhibits liquid crystal formation (16).

Figure 3 shows scattering distribution of small droplets in the range of 1-2 μm in the middle phase after the system left for 3 weeks indicating that the formation of macroemulsion was present along with microemulsion. It was found that the solution became absolutely transparent and the small droplets disappeared after the systems left for a few months. The finding reveals that as a result of shaking during preparing a microemulsion system, macroemulsion occurs. It is quite stable for a period of time but eventually disappears. The stability of macroemulsion is governed by the rate of coalescence and the free energy of the emulsion film (17). Since the studied systems were prepared with very high concentration of the surfactants, the solutions became very viscous resulting in decreasing rate of coalescence. This is an explanation why the macroemulsion formed in the present studied systems were quite stable and remained for a few weeks.

Water content in microemulsion and excess oil phases. Figure 4 shows the water content in an excess oil phase and a middle phase at different salinity of formulations S1, S2 and S3. The results showed the same trends for all systems that the higher salinity, the lower water content in the middle phase was obtained but the higher water content was found in the excess oil phase. In addition, when comparing these three systems at any given salinity, the more hydrophilic environment corresponding to a higher ADPODS concentration, the higher water content was found obviously in the middle phase. This result indicates that adding ADPODS enhances water solubility in the middle phase since the system becomes more hydrophilic.

Equilibrium interfacial tensions. Table 3 shows the IFT* values of all three formulations S1, S2 and S3 compared to the IFT values of oil in water microemulsion and excess oil phase ($\text{IFT}_{\text{w/m/o}}$) and of excess water phase and excess oil phase ($\text{IFT}_{\text{w/o}}$). IFT* is defined as interfacial tension at optimum where $\text{IFT}_{\text{o/m}}$ and $\text{IFT}_{\text{w/m}}$ are equal. The experimental results showed that either IFT* or $\text{IFT}_{\text{w/m/o}}$ at 1.75% NaCl or $\text{IFT}_{\text{w/o}}$ at 5% NaCl for all studied formulations were in the same range of 10^{-2} to 10^{-1} mN/m. The IFT values obtained from the present study quite agree with the literatures (6,11) that a system with triolien generally has a higher IFT

than the system with a hydrocarbon oil due to the nature of triolien that is more difficult to form microemulsion.

Dynamic interfacial tensions in the washing bath. As mentioned in our previous studies (11,12), IFT values after a system reaches equilibrium and dynamic IFT values during the washing cycle were found to be different due to the changes of oil/water ratio and surfactant concentration. Therefore, the dynamic IFT of the washing solutions prepared from the studied formulations S1, S2 and S3 were determined to monitor a real situation happening during the wash step. The active concentration of the washing solution was 0.25% by diluting the studied formulations and NaCl was added as variable parameter.

Figures 5-7 show plots of IFT at different salinities as a function of time for the three formulations of S1, S2 and S3, respectively. The similar trend was observed for all systems that IFT reached equilibrium within 10 minutes or about a half of the washing cycle. In addition, most of IFT values were in the range from 0.1 to 1.0 mN/m, except the IFT values from the formulation S1 that were mostly higher than 1.0 mN/m. The result indicates that either an addition of ADPODS or increasing salinity lowers IFT of the system. The presence of the counter ions from adding salt results in reducing repulsive forces between the anionic surfactant molecules. As a result, there are more amounts of the surfactant molecules arranging at the interface between the washing solution and triolien and so the interfacial tension of the system is reduced. Recently, Acosta and coworkers (18,19) revealed that the presence of hydrophilic linkers in a system tended to decrease the interfacial thickness and interfacial rigidity, but to increase the coalescence rate of the system. It is believed that adding ADPODS in the studied system behave similar to a hydrophilic linker to decrease interfacial rigidity at the interface between oil and the surfactant solution which leads to lowering IFT values.

A dynamic IFT value of the system containing the commercial liquid detergent (CP) was also found to have a very low value and reached equilibrium within a few minutes. The dynamic IFT values of the washing solution prepared from the three formulations at any salinity were relatively higher than all IFT value at equilibrium obtained from the phase study at an oil/water ratio of 1:1 as shown in

Table 3. This is due to the difference in surfactant concentration and a water to oil ratio as mentioned previously.

Detergency performance: effect of salinity. Three systems prepared from three formulations S1, S2 and S3 were performed for the detergency experiment. The active concentration of the washing bath was kept constant at 0.25% with various salinities. Unlike the previous study with the hydrocarbon oils e.g. hexadecane and motor oil (11), two maximum detergency peaks were obtained for all studied systems in the salinity range from 0.05 to 12% NaCl (see Figure 8 and Table 4). The result showed that the higher the hydrophilicity of the system, the higher the salinity was required for the maximum detergency (D_{max}). Interestingly, triolien removal at the second maximum detergency peak was higher than that at the first maximum detergency peak in all three formulations

Figures 9-11 illustrate the profiles of triolien removal and IFT at different salinities of the systems S1, S2 and S3, respectively. For all systems, the first maximum detergency (D_{max1}) at a low salinity was lower than the second maximum detergency (D_{max2}) at a high salinity. The D_{max2} was found to correspond to a lower IFT value than that of the D_{max1} , which agreed with most previous studies that the maximum detergency correlates to the minimum IFT of the system. From this result of the present study, it may be concluded that for the mixed surfactant system with triolien a lower IFT value does not always lead to a better detergency performance. However, the observation showed that to obtain 70% or higher triolien removal for any formulation, the IFT values between the oil and washing solution has to be lower than 1.0 mN/m. This finding indicates that IFT is still an important parameter influencing on detergency performance. On the other words, it may be concluded that it is not only a reduction of IFT to enhance oil removal, but other parameters may involve the cleaning process as mentioned by Thompson (10). He showed the occurrence of the two maximum detergency peaks for triolien. In addition, the paper pointed that the D_{max} did not always correspond to the minimum interfacial tension (IFT_{min}). Thompson proposed that besides IFT_{min} , contact angle as well as the adhesive and cohesive work between oil and substrate were believed to influence the oil removal.

Maximum detergency at low interfacial tension. From our previous study on two hydrocarbon oils of hexadecane and motor oil (20), we proposed the mechanism of oil removal related to the adsorption of surfactant on substrate which causing spreading of the oil into fiber bundle when the system has ultralow IFT at middle phase. During the rinse step with deionized water, most of surfactant molecules and counter ions adsorbed will be desorbed causing an increase in IFT at the interface. Consequently, adsorbed oil will be gradually detached from the fabric surface by the snap-off mechanism. From our previous result, it can be concluded that most oil removal occurs in the wash step. However, if the system is operated in the Winsor 's type III microemulsion or middle phase region, oil removal in the rinse step is as high as that in the wash step. In addition, for a highly hydrophilic oil, motor oil, the oil is mostly removed in the rinse step instead of the wash step. In this present work, similar experiments were performed for the system S1 and S2. The result of IFT between the oil and the washing solution before and after the wash step is shown in Figure 12. The result obviously shows a drastic increase in IFT of the after-wash solution at the $D_{\max 2}$ for the case of S1 system where the system is located in the middle phase. This result indicates that a significant amount of surfactant adsorbed on fabric surface during the washing step. Thus, the IFT value of the washing solution and the oil after the wash step became higher than that before the wash step.

In addition, an experiment on detergency was conducted by using two different rinsing methods. Instead of D.I. water, brine as the same concentration of NaCl as in the washing solution was used as rinse water. As expected, we found that at high salinity where low IFT occurred in the wash step, failed to reach the maximum detergency when brine was used as rinse water. While at low salinity and relatively high IFT value where the $D_{\max 1}$ occurred, the detergency result still maintained its performance even rinsing with brine (see Figure 13). This finding show that spreading effect occurred in the case of the second maximum detergency at high salinity and hence low IFT. The detail of mechanism of oil removal at high salinity due to spreading was explained in more detail in our previous study (20). However, it is quite obvious that the $D_{\max 1}$ that appeared at low salinity was occurred by other mechanism.

Maximum detergency at low salinity. As mentioned earlier, our studied systems S1, S2 and S3 gave also another maximum detergency for triolien removal at low salinity where the detergency result was found not to be corresponded to low IFT. The reason for maximum detergency at this low salinity is still unable to explain from IFT values. However, it was significantly that salinity has an effect on another parameter that influences detergency performance. Since the results from this present study are distinctive from the previous studies with hydrocarbon oil, we need to consider in more details of this present studied systems. In our studied systems S1, S2 and S3, Tergital 15-S-5 or secondary alcohol ethoxylate, a nonionic surfactant was used in the formulations. Its property on water solubility is defined as dispersible. When Tergital 15-S-5 is mixed with AMA, and with or without ADPODS at suitable proportion, the clear homogeneous solution was obtained. The adding of salinity at a certain amount to these mixed surfactants enhances the solubility and reducing its viscosity. However at a given temperature, we found that an adding of salt beyond a certain amount, the phase separation occurred. This phenomenon can be referred as a cloud point temperature where phase separation occurs for a system of nonionic surfactant in aqueous solution (21).

Cloud point is the highest temperature in which a nonionic surfactant solution is clear. At the cloud point temperature and for the temperature above cloud point temperature, the surfactant solution becomes turbid or cloudy due to the drastic increase in the size of the micelle. Phase separation then occurs in the surfactant solution, consisting of two phase namely; coacervate phase and dilute phase. When an ionic surfactant is added to a nonionic surfactant system, it tends to increase the cloud point of the system (22,23). On the other hand, adding salt to a system of mixed nonionic and anionic surfactants leads to a decrease in cloud point temperature (18,22,24). For our studies systems, Tergital itself is only dispersible in water but the introduction of AMA and ADPODS improves the system become water soluble and hence clear solution is obtained at a certain condition. At a given temperature, when salinity scan is conducted in these mixed surfactant systems, the system behaves similar to temperature scan as did in a nonionic surfactant. Hence the phase separation occurs at a certain salinity for each system. Coincidentally, the salinity where the phase separation occurred in each studied formulation is just about

the same salinity where the $D_{\max 1}$ result occurred (see the observation data in Table 5). Consequently, we could predict that the phase separation due to the salinity scan may be one of parameter influence detergency performance. However, from the experimental data available in this present study, we probably only propose the relation of phase separation to detergency result at low salinity. Since there is not experimental data at present to prove this hypothesis, the future study will be explored in more details for explanation of this mechanism.

NOMENCLATURE

AMA	dihexyl sodium sulfosuccinate
ADPODS	alkyl diphenyl oxide disulfonate
TM-5	Tergital15-S-5 (secondary alcohol ethoxylate)
CP	commercial liquid detergent
IFT	interfacial tension (mN/m)
IFT*	interfacial tension at the optimum condition
S*	salinity at the optimum condition
Om	water in oil microemulsion
Wm	oil in water microemulsion
D.I.	deionized water

Subscripts

O	excess oil phase
W	excess water phase
M	middle phase

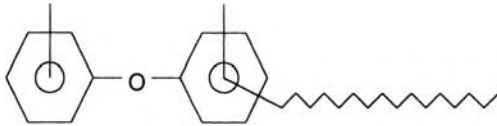
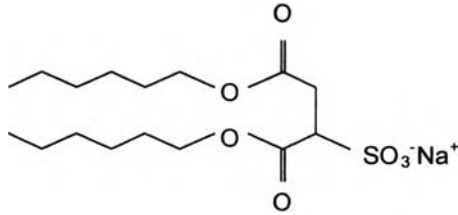
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TABLE 1
Properties of Surfactants Used in the Study

Chemical Name	Chemical Formula/Structure	MW	HLB
Alkyl diphenyl oxide disulfonate, ADPODS (Dowfax 8390)	SO_3^-Na^+ SO_3^-Na^+ 	642	> 40*
Sodium dihexyl sulfosuccinate acid (AMA)		444	
Secondary alcohol ethoxylate (Tergital 15-S-5)	$\text{CH}_3(\text{CH}_2)_{9-11}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	428.6	10.3

Note * For Dowfax 8390, the HLB is not available, however, it is reported that its HLB is higher than sodium dodecyl benzene sulfonate whose HLB is around 40. (ref.25)

TABLE 2
Three Formulations of Mixed Surfactants Used in Phase Study

System	Concentration (wt%)			Total (wt%)
	Tergitol 15-S-5	AMA	ADPODS	
S1	20.75	9.70	0	30.45
S2	20.75	9.70	1.93	32.38
S2	20.75	9.70	3.86	34.13

Table 3
Equilibrium Interfacial Tensions between Phases and at Optimum Salinity of the Studied formulations at a Water to Oil Ratio of Unity

Formulations	IFT* (mN/m)	S* (%NaCl)	IFT _{w/mO} (mN/m)	IFT _{w/O} (mN/m)
S1	0.072	4.1	0.122	0.179
S1	0.082	4.5	0.152	0.142
S3	0.077	6.2	0.192	0.162

Note:

- IFT* is IFT at optimum where IFT_{O/M} equals IFT_{w/M} (or at S*)
- S* is salinity at optimum where IFT* exists.
- IFT_{w/mO} is an IFT between O/W microemulsion (Wm) and oil phase of the systems at 1.75 % NaCl
- IFT_{w/O} is an IFT between excess water and excess oil phases of the systems at 5 % NaCl

TABLE 4
Detergency Results Relating to Interfacial Tension (IFT) and Salinity at the Two
Maximum Detergency Regions with Three Different Formulations

Parameters	Formulations		
	S1	S2	S3
At the first maximum detergency (D_{max1})			
• IFT* (mN/m)	2.038	0.674	0.438
• Salinity (%NaCl)	0.10	0.50	1.00
• Oil removal (%)	60.2	75.8	72.7
At the second maximum detergency (D_{max2})			
• IFT* (mN/m)	0.473	0.184	0.165
• Salinity (%NaCl)	4.25	8.00	10.0
• Oil removal (%)	75.1	79.8	75.0

Note * IFT is interfacial tension between washing solution and dyed triolien

Table 5

The Appearance of the Washing Solution Containing 0.25% Active Concentration of the Mixed Surfactant at Different Salinities at 30°C of the Three Formulations

% NaCl	Formulation		
	S1	S2	S3
0.1	Bluish homogeneous	Bluish homogeneous	No data
0.25	Phase separate with a very small volume of bluish coacervate phase	Bluish homogeneous	No data
0.5	Volume of coacervate phase reduced	Bluish homogeneous	Bluish homogeneous
1.0	Same as 0.5% NaCl	Phase separate with a very small volume of bluish coacervate phase	Bluish homogeneous
1.75	Same as 0.5% NaCl	Volume of coacervate phase reduced	Bluish homogeneous
3.0	Same as 0.5% NaCl	Same as 1.75% NaCl	Phase separate with a very small volume of bluish coacervate phase
4.25	Same as 0.5% NaCl	Same as 1.75% NaCl	Volume of coacervate phase reduced
6.25	No data	Same as 1.75% NaCl	Same as 4.25% NaCl
8.0	No data	Same as 1.75% NaCl but with clear coacervate phase	Same as 4.25% NaCl
10.0	No data	Same as 8.0% NaCl	Same as 8.00% NaCl but with clear coacervate phase

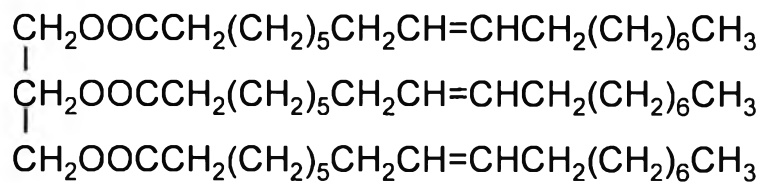


FIG. 1 Formula structure of triolien

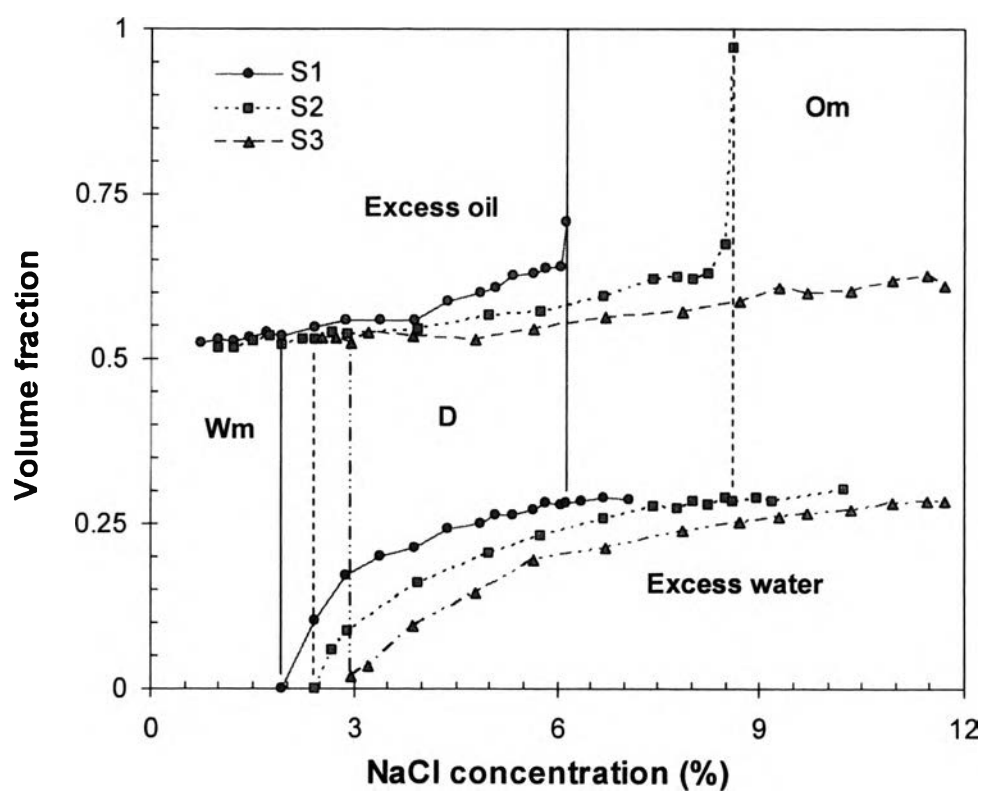


FIG. 2 Phase diagram of the studied systems S1, S2 and S3 at 30 °C with salinity scan (Wm is oil in water microemulsion, Om is water in oil microemulsion and D is middle phase).

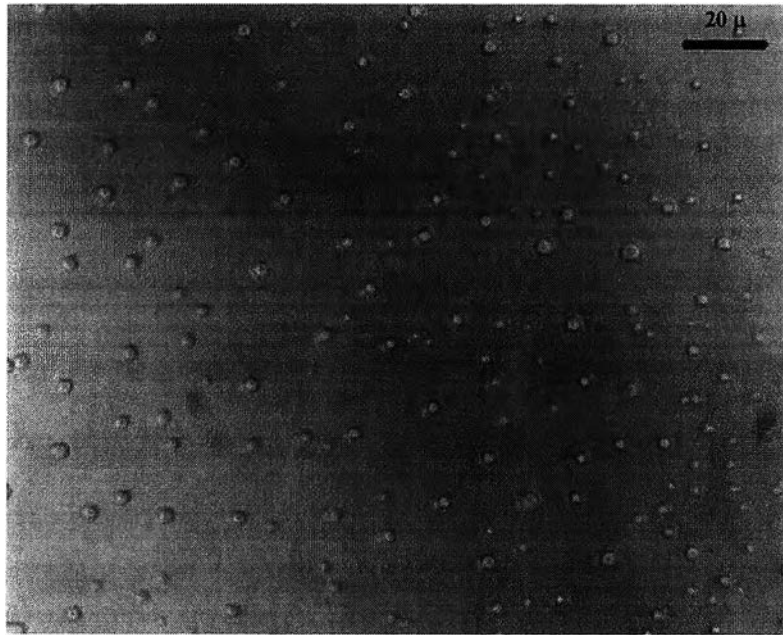


FIG. 3 Image of the middle phase of the system S1 at 6% NaCl, illustrates small drops of stable macroemulsion after left for 3 weeks.

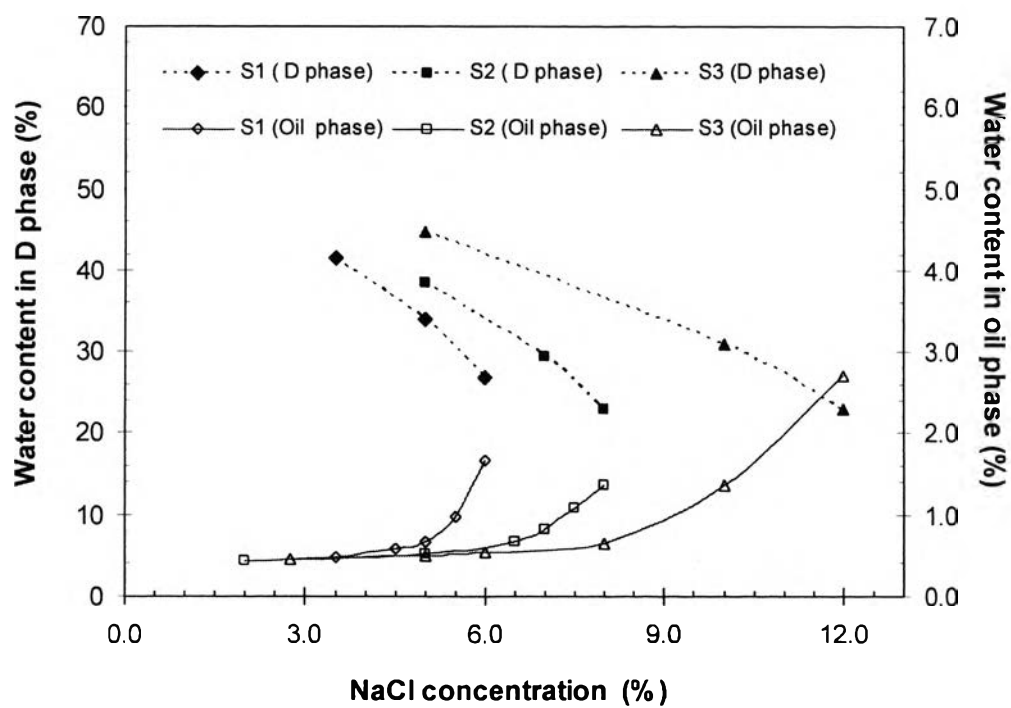


FIG. 4 Water content (%) in the middle phase and oil phase at different salinities of the studied systems S1, S2 and S3; where D is the middle phase.

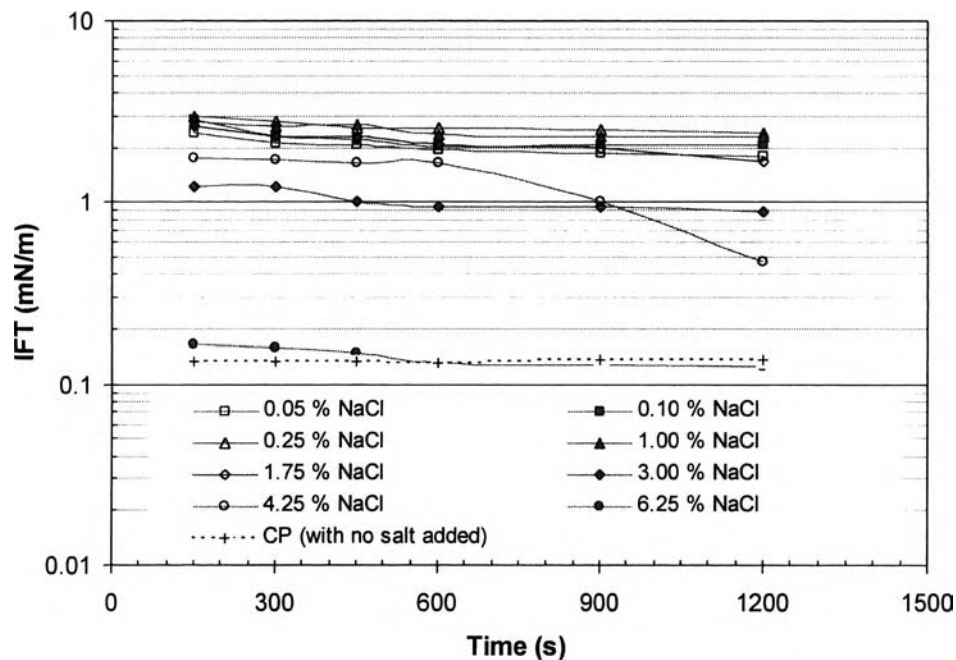


FIG. 5 Dynamic IFT of the washing bath (0.25% total active concentration of formulation S1) and triolien at different salinities compared to CP (commercial liquid detergent).

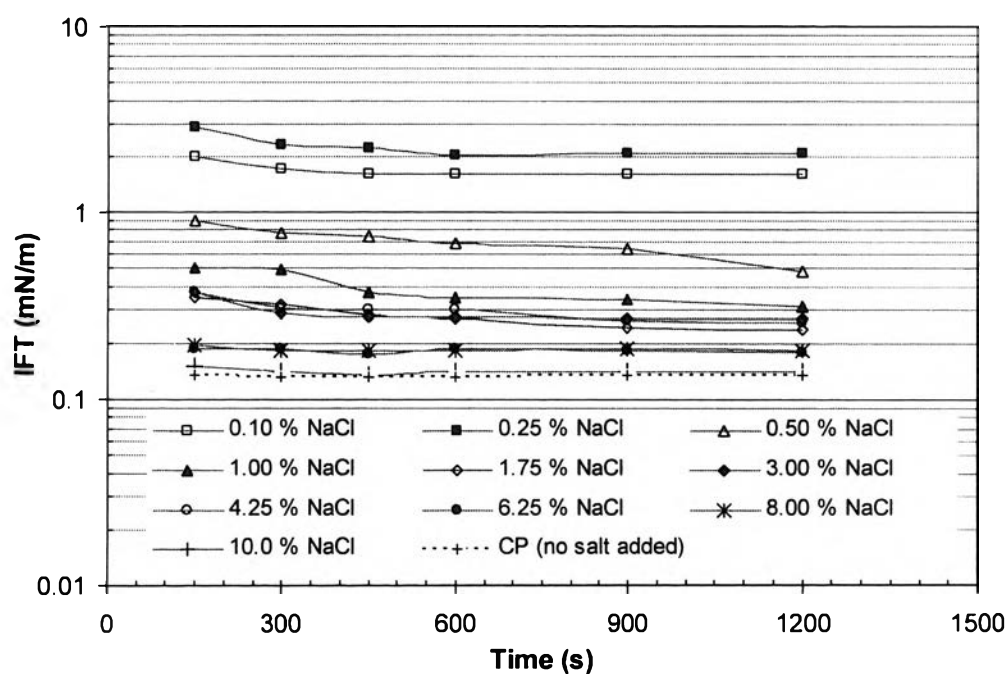


FIG.6 Dynamic IFT of the washing bath (0.25% total active concentration of formulation S6) and triolien at different salinities compared to CP (commercial liquid detergent).

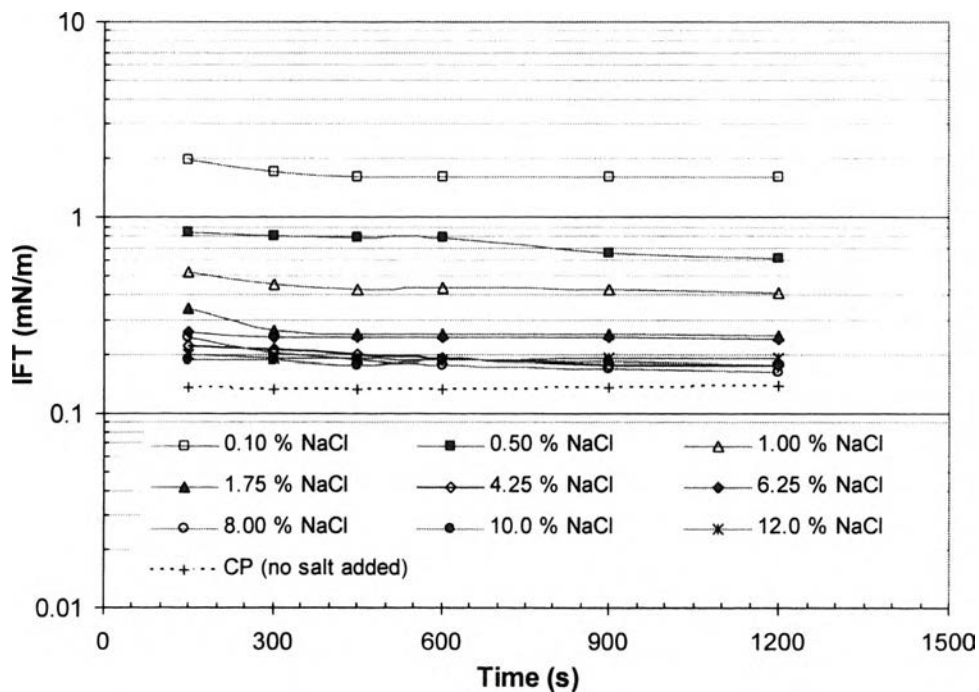


FIG. 7 Dynamic IFT of the washing bath (0.25% total active concentration of formulation S3) and triolien at different salinities compared to CP (commercial liquid detergent).

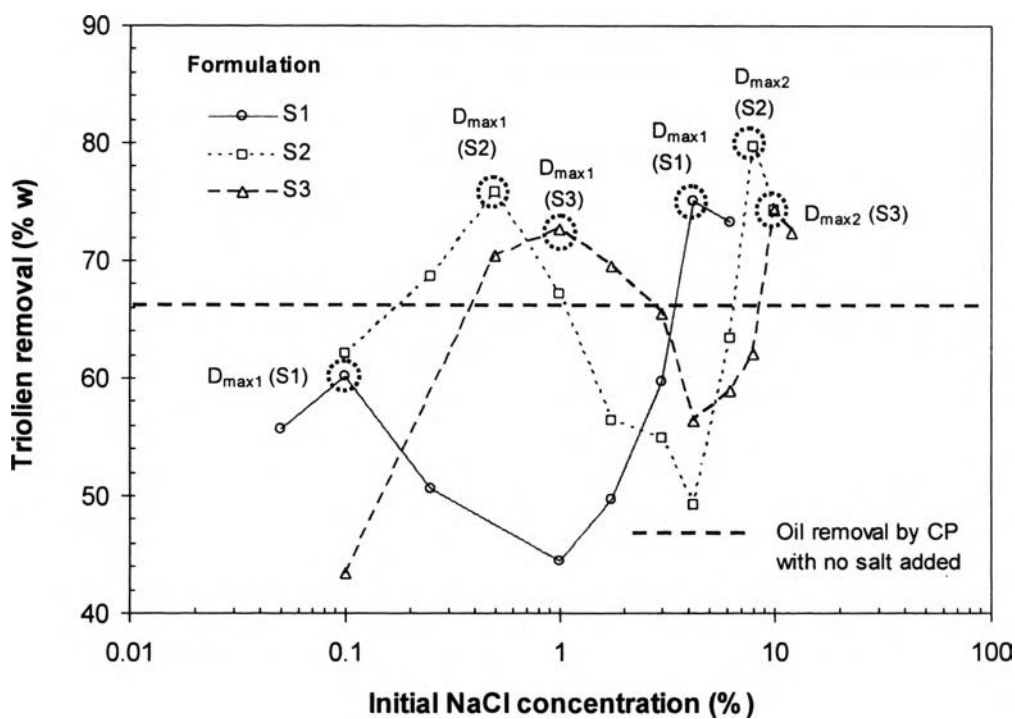


FIG. 8 Triolien removal as a function of salinity at 30 °C of three formulations where D_{max1} and D_{max2} are maximum detergency peaks.

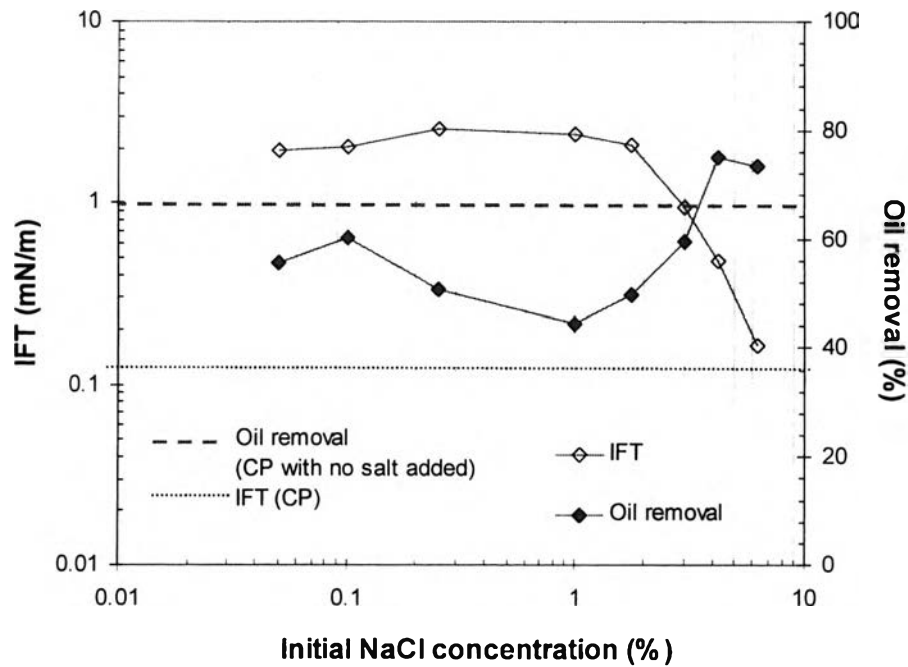


FIG. 9 Triolien removal with formulation S1 compared to the commercial liquid detergent (CP) and the interfacial tensions between the oil and washing solution at various salt concentrations.

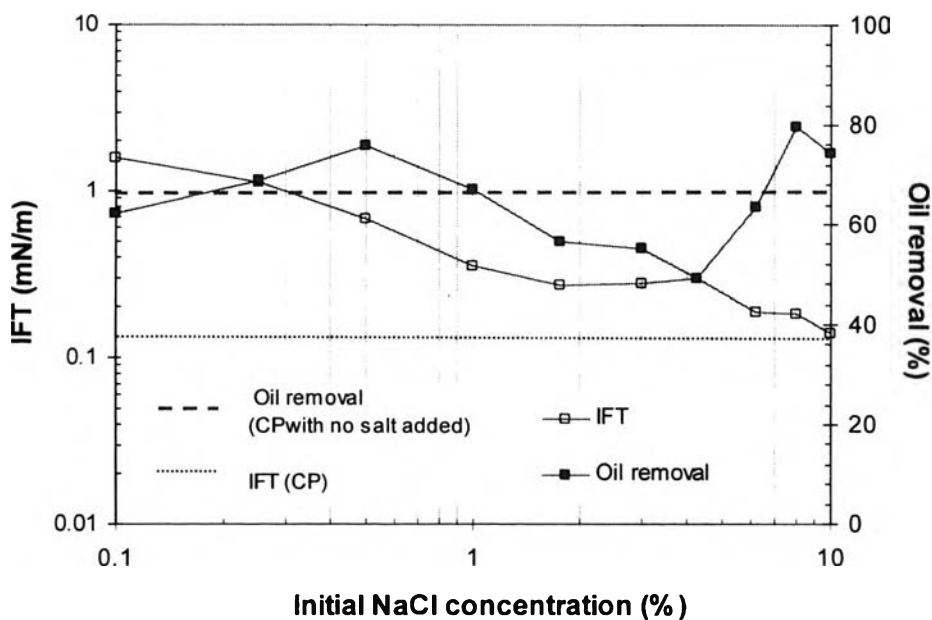


FIG. 10 Triolien removal with formulation S2 compared to the commercial liquid detergent (CP) and the interfacial tensions between the oil and washing solution at various salt concentrations.

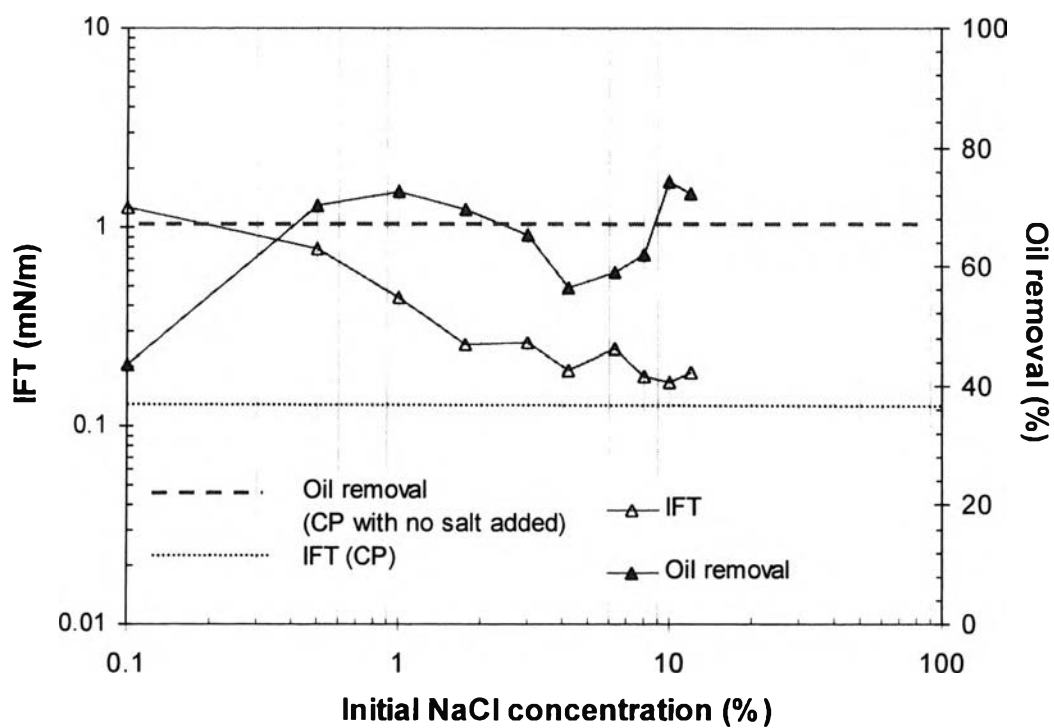


FIG. 11 Triolien removal with formulation S3 compared to the commercial liquid detergent (CP) and the interfacial tensions between the oil and washing solution at various salt concentrations.

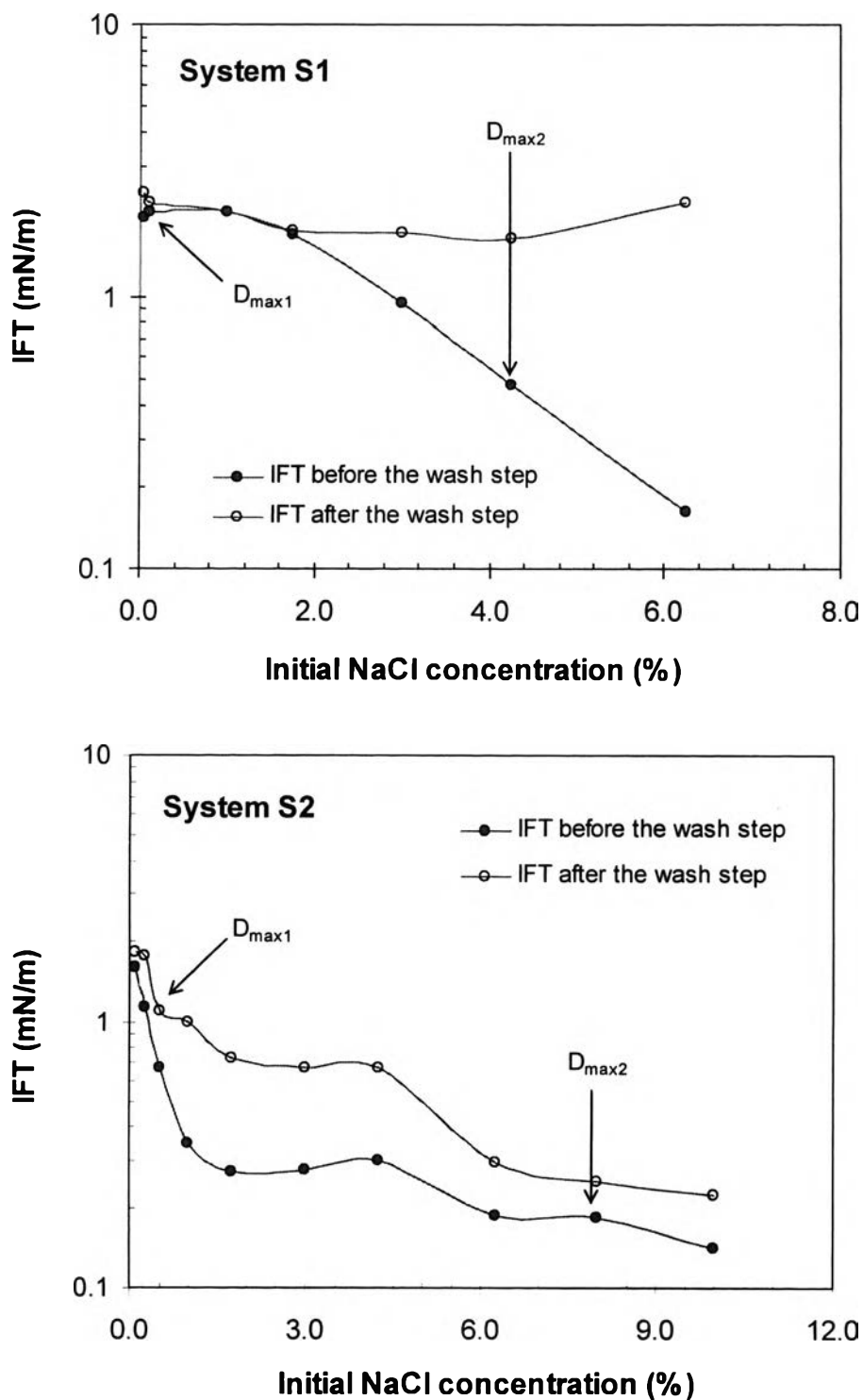


FIG. 12 Comparison of interfacial tension with two formulations S1 and S2 at different salinities before and after the wash step

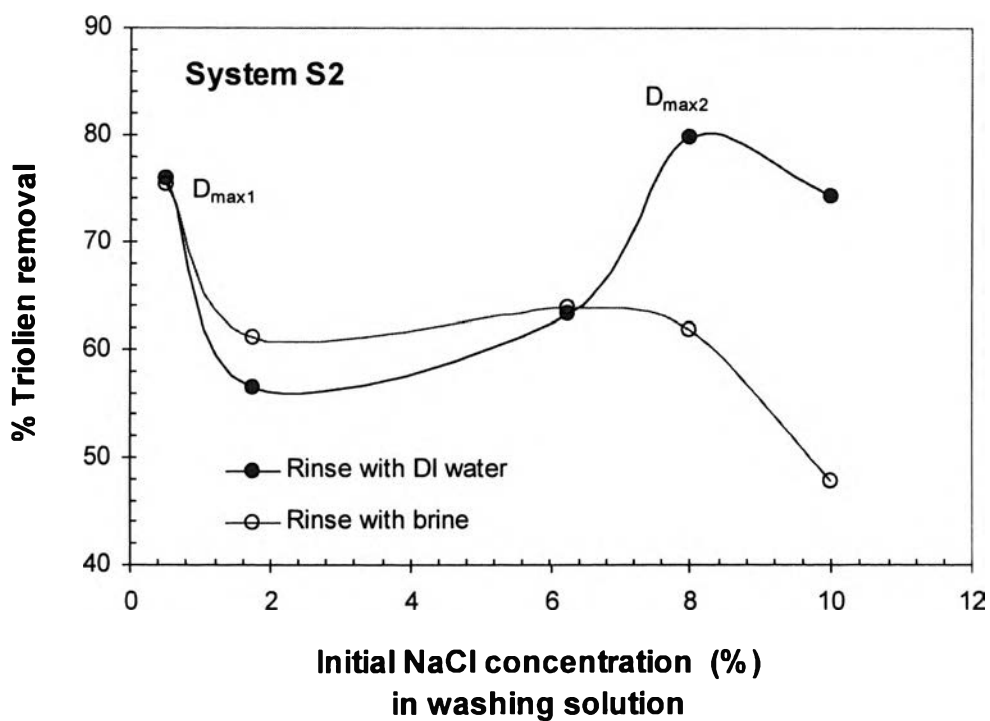
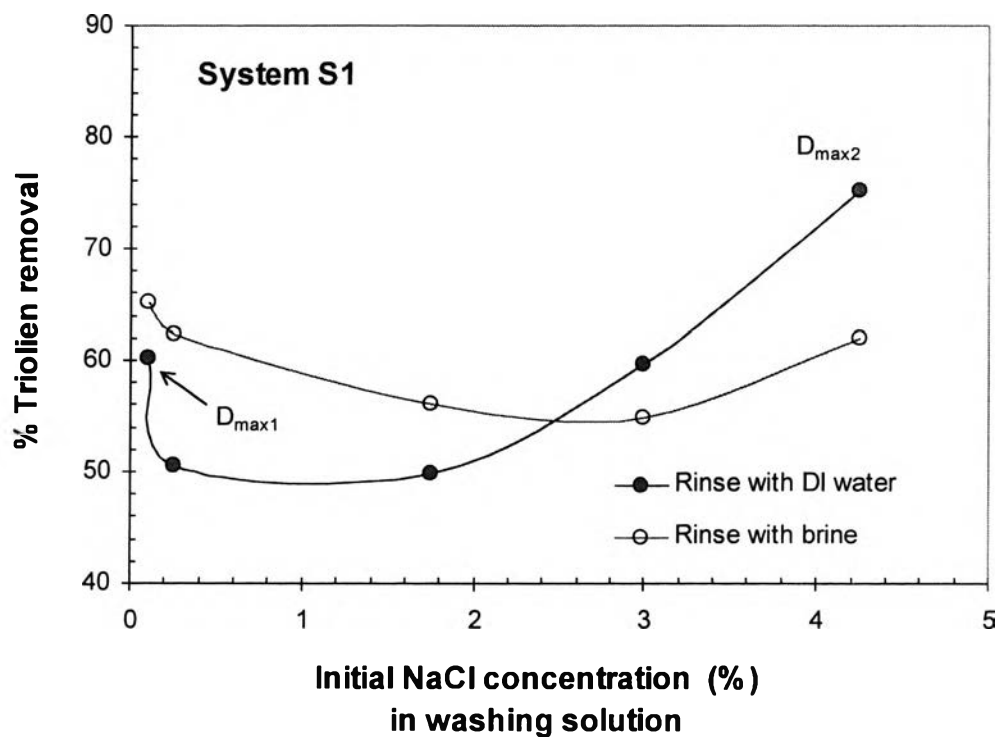


FIG. 13 Comparison triolien removal after the washing process with two different formulations S1 and S2 and two rinse methods of D.I. water and brine.