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FORMATION, CHARACTERIZATION AND APPLICATION OF TRIGLYCERIDE MICROEMULSIONS USING EXTENDED SURFACTANTS

A DISSERTATION APPROVED FOR THE
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BY

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DEDICATION

This dissertation is dedicated to my wife Dung Le and my daughter Annie Phan.

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ABSTRACT

Triglycerides are among the most challenging oils to microemulsify due to their unique structure of a bulky polar ester head and three long hydrocarbon chains. Among the published work on triglyceride microemulsions, the use of extended surfactants provides ultralow interfacial tension (IFT) and very high solubilization enhancement. However, the impacts of triglyceride and extended surfactant structure on their ability to achieve low IFT and high solubilization capacity have not been addressed fully in the literature. Applications of extended surfactant microemulsion systems are also very limited. The primary goal of this dissertation is to better understand the impacts of triglyceride structure and extended surfactant structure on their behavior in triglyceride microemulsion systems and to demonstrate the viability of using extended surfactant microemulsion system in vegetable oil detergency application.

The results show that with increasing degree of unsaturation (more double bonds), surfactant interactions with the triglycerides is weaker requiring higher optimum salinity and resulting in higher interfacial tension values. Effects of ester groups and chain length of triglyceride are also discussed and the Equivalent Alkyl Carbon Number (EACN) of the studied triglycerides and vegetable oils are reported. With regard to structure of extended surfactants, the results show that branching of hydrocarbon tail of extended surfactants lowers optimum salinity and IFT values as well as enhances triglyceride solubilization through middle phase microemulsion formation.

The results also show that ultralow IFTs with vegetable oils can be achieved using extended surfactants with eight polypropylene oxide (PO) groups or more. This work also demonstrates that a microemulsion-based extended surfactant formulation is a highly viable approach for vegetable oil detergency with high oil removal efficiencies achieved at low surfactant concentration and at reduced wash temperature, an encouraging step toward “green” detergent products.

CHAPTER 1

Introduction

Triglycerides and Triglyceride-related Applications

Triglycerides are the main components in vegetable oil, fish oil and algae oil. Triglycerides are esters of a glycerol molecule and three fatty acids. The three fatty acids may be the same or different and can be saturated or unsaturated. The hydrocarbon chains of the fatty acids can be as long as 24 carbons and are non-branched [1]. When the three fatty acids in a triglyceride molecule are the same, the nomenclature of triglycerides is often referred to by the hydrocarbon chain length and the number of double bonds of the fatty acid. For example, triolein, an ester of a glycerol and three oleic acids (with 18 carbons and one double bond) is referred to as triolein (C18:1). A list of common triglycerides with their molecular structures and nomenclatures is presented in Appendix A.

Traditionally, triglycerides have been used as important lipid sources in human diet and for cooking purposes. Recently, with the trend toward environmentally sustainable development and natural resource conservation, triglycerides have been exploited as renewable materials for biodiesel production [1], raw materials for industrial processes [2], and as natural ingredients in cosmetic and pharmaceutical products [3-4]. These applications require unique properties which can be achieved through microemulsion systems.

Microemulsion Background

Microemulsions are thermodynamically stable mixtures of oil and water produced using surfactant formulations [5]. Microemulsions have gained special attention because of the unique properties they provide such as thermodynamical stability, transparency, ultralow interfacial tension (IFT) and high solubilization ability [5-7]. Our current understanding of microemulsions has evolved from the early work of Winsor [9]. Winsor classified microemulsion systems into three categories: known as Winsor Type I, II and III microemulsions. In Winsor Type I microemulsions, the oil is solubilized in normal micelles in the water phase. In Winsor Type II microemulsions, water is solubilized in reverse micelles in the oil phase. Winsor Type III microemulsions sometimes referred to as middle phase microemulsions, can be envisioned as both water and oil swollen micelles in a bi-continuous structure [6, 7].

Winsor explained the phase transition using the Winsor R ratio as defined in its simplest form $R= A_{SO\ net} / A_{SW\ net}$, where $A_{SO\ net,}$ $A_{SW\ net}$ are the net interaction energies between the surfactant molecule and the oil and water phases, respectively [6-9]. According to Winsor, the system has the highest solubilization capacity when the R ratio approaches unity, which indicates a balance between the interactions of the surfactant with the oil phase and with the water phase. The system is Winsor Type I when $A_{SO\ net} < A_{SW\ net}$ and is Winsor Type II when $A_{SO\ net} > A_{SW\ net}$. Conditions when R=1 are called optimum conditions and are defined as where IFT is minimum (IFT*) and solubilization parameter is maximum (SP*) [6-7]. Although R is defined to be unity at optimum conditions, surfactants with different values of $A_{SO\ net}$ and $A_{SW\ net}$ can produce different optimum conditions. Therefore, by comparing optimum conditions of a surfactant system with different oils, one can evaluate the relative interactions of the surfactant system with each kind of oil. For example, comparing the microemulsion systems of two oils with the same anionic surfactant system, the oil that requires higher optimum salinity (S*- salinity at with IFT* and SP* are achieved) indicates a weaker interaction with the oil phase because more electrolyte is required to neutralize the negative charged head group, thus decreasing the interaction with the water phase to bring the R ratio to unity. Additional details on microemulsion fundamentals and approaches for quantifying individual interaction energies can be found in the excellent review paper and book by Salager et al [6] and Bourrel et al [7].

Triglyceride microemulsion

Despite the advanced understanding gained from the extensive microemulsion work with n-alkane oils or chlorinated hydrocarbons, triglycerides remain the most challenging oil to microemulsify due to their unique structure of a bulky polar ester head and three long hydrocarbon chains. How the structure of triglyceride molecules affects its ability to achieve low interfacial tension and high solubilization ability in microemulsion systems have not been addressed fully in the literature.

Triglyceride microemulsion formation has been reported using different approaches such as co-oil addition, alcohol addition, non-ionic surfactants at high temperature, and extended surfactants with linkers [10-20]. Among the published work on triglyceride microemulsions, the use of extended surfactant in triglyceride microemulsion [13, 19-21] has gained special interest because of the ability of extended surfactants to provide ultralow IFT and very high solubilization enhancement. Extended surfactants were first introduced in 1995 by Minana-Perez et al. [13]. The concept of extended surfactants originated from the effort to try to increase the surfactant-oil interaction by inserting a number of polypropyleneoxide (PO) groups between the head group and the tail of the surfactant. Although previous work has demonstrated that extended surfactants can provide ultralow IFT and high solubilization capacity for triglyceride microemulsions [13, 19-20], limited information is available on how the structure of extended surfactant molecules affect their ability to achieve low IFTs and to form microemulsion with triglyceride oils. Understanding these effects is of great importance for optimizing extended surfactant triglyceride microemulsion systems for various applications and is the focus of this work.

Research Questions and Goals

Based on the knowledge gap stated above, this dissertation is dedicated to answering the research question of how molecular structures of triglycerides and extended surfactants impact their ability to achieve low IFT and to form microemulsions. In addition, this work also reveals whether extended surfactant-based triglyceride microemulsion is a viable approach for vegetable oil detergency.

The primary goal of this dissertation is to better understand the effects of triglyceride structure and extended surfactant structure on their behavior in triglyceride microemulsion systems. The secondary goal is to demonstrate the viability of using extended surfactant microemulsion system in applications. The primary goal is evaluated in Chapters 2 and 3 while the secondary goal is evaluated in Chapter 4.

Overview of Chapters

In Chapter 2, the effect of triglyceride molecular structure on surfactant-oil-water interactions was studied by evaluating optimum salinity and dynamic interfacial tensions of an anionic extended surfactant and triglyceride oils with different chain length and degree of unsaturation. The results reveal an important finding that with increasing degree of unsaturation (more double bonds), triglyceride oils acts as more hydrophobic oils, reflected by a higher salinity required to achieve optimum condition and also resulting in higher interfacial tension values. This might be a result of weaker surfactant-oil interactions due to steric hindrance. Ester groups in triglyceride molecules are found to reduce oil hydrophobicity. Increasing chain length of triglyceride leads to increased optimum salinity but causes little change in IFT values. The Equivalent Alkane Carbon Number (EACN) of the individual triglycerides and vegetable oils are also determined.

In Chapter 3, the impact of extended surfactant structure (e.g. number of PO groups, length and branching nature of the hydrocarbon chain) on microemulsion phase behavior and IFT values with triglyceride oils was evaluated. The results show that extended surfactants with branched hydrocarbon tails have lower optimum salinity and IFT values compared to linear tail extended surfactants with the same number of carbon. Branching of hydrocarbon tail was also found to enhance triglyceride solubilization through middle phase microemulsion formation. The importance of hydrocarbon tail branching in extended surfactant microemulsion is consistent with the finding of steric effects caused by degree of unsaturation. The results also show that ultralow IFTs with vegetable oils can be achieved using extended surfactants with eight polypropylene oxide (PO) groups or more.

Chapter 4 demonstrated the viability of using extended surfactant in vegetable oil detergency. For highly hydrophobic oily soils such as vegetable oils, formulating surfactant systems to achieve low IFT is a challenge. Based on the findings from Chapter 3, a branched extended surfactant was selected for the detergency test. The surfactant was able to form microemulsion and achieve ultralow IFT with canola oil at room temperature of 25^{o}C. The results showed that good canola oil detergency (>80%)

was achieved at 25^{o}C at concentrations as low as 125 ppm. The results also reveal that maximum detergency (95%) was achieved in the Type II microemulsion region. These results demonstrate that a microemulsion-based extended surfactant formulation is a viable approach for vegetable oil detergency at room temperature, an encouraging step toward "green" detergent products using low surfactant concentrations and reduced wash temperature.

Finally, Chapter 5 recaps important findings of this dissertation which significantly contribute to the advancement of our understanding of extended surfactant triglyceride microemulsions as well as in practical application of extended surfactants.

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CHAPTER 2

A Systematic Study of Triglyceride Molecular Structure Effects on Optimum Formulation[1]

Abstract

In this work, the effects of triglyceride molecular structure on surfactant-oil-water interactions were evaluated by comparing optimum salinity and dynamic interfacial tensions of an anionic extended surfactant and triglyceride oils with different chain length and degree of unsaturation. The results show that with increasing degree of unsaturation (more double bonds), surfactant interactions with the triglycerides is weaker requiring higher optimum salinity and resulting in higher interfacial tension values. Effects of ester groups and chain length of triglyceride are also discussed and the EACN of the studied triglycerides and vegetable oils are reported.

Key words: triglyceride, vegetable oil, microemulsion, oil hydrophobicity, EACN, extended surfactant

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[1] This chapter was accepted in August 2009 to be published in Journal of Surfactants and Detergents under title of "Effects of Triglyceride Molecular Structure on Optimum Formulation of Surfactant-Oil-Water Systems".

Introduction

Triglycerides are the main components in vegetable oils [1-2]. Traditionally, triglycerides have been used as important lipid sources in human diet and for cooking purposes. Recently, with the trend toward environmentally sustainable development and natural resource conservation, triglycerides have been exploited as renewable materials for biodiesel production [3], raw materials for industrial processes [4], and as natural ingredients in cosmetic and pharmaceutical products [5-6]. All of these applications require low interfacial tension (IFT) and high solubilization of triglycerides which can be achieved through microemulsion systems.

Triglycerides are esters of glycerol and three fatty acids, which may have the same or different alkyl lengths and can be saturated or unsaturated. The hydrocarbon chains of the fatty acids can be as long as 24 carbons and are non-branched [7]. This configuration of a bulky polar head and three long hydrocarbon chains makes triglycerides among the most challenging oils to microemulsify, especially as compared to *n*-alkane oils or chlorinated hydrocarbons which have been studied extensively in microemulsion studies. Although triglyceride microemulsion systems have been reported elsewhere [8-13], the impact of triglyceride structure on their interactions with surfactants and water in microemulsion systems is not yet well understood.

Surfactant-oil-water interactions can be qualitatively evaluated using the Winsor R ratio concept as shown in Eq. 2-1 [14-16], where $A_{SO\ net}$ = net surfactant-oil interaction energy and $A_{SW\ net}$ = net surfactant-water interaction energy. For example, comparing optimum conditions (R=1) of two oils with the same anionic surfactant system, the oil that requires higher optimum salinity (S*- salinity at which minimum IFT* and highest solubilization parameter SP* are achieved) indicates a weaker surfactant interaction with the oil phase because more electrolyte is required to decrease the surfactant interaction with the water phase and thus reach optimum condition. Another method of evaluating the surfactant-oil-water interactions is use of the Equivalent Alkyl Carbon Number (EACN) whereby oils are assigned EACN values to indicate their "hydrophobicity" relative to *n*-alkanes [17-24]. In this work, the effect of triglyceride molecular structure on oil hydrophobicity was evaluated by comparing optimum conditions (S* and IFT*) of various triglycerides having different chain lengths and degrees of unsaturation.

$$R = \frac{A_{SO\,net}}{A_{SW\,net}} \tag{2-1}$$

Experimental Procedures

Materials: *n*-alkane oils were purchased from Sigma-Aldrich (St. Louis, MO) with purity > 99%. All synthetic triglyceride oils and methyl oleate were purchased from Nu-Check Prep, Inc. (Elysian, MN) with the purity > 99%. All the unsaturated triglycerides and methyl oleate are in *cis*-configuration. Peanut oil and olive oil were purchased from Sigma-Aldrich (St. Louis, MO). Canola oil was purchased from a local store. Sodium chloride (> 99% purity) was purchased from Sigma-Aldrich (St. Louis, MO).

The surfactant used in this research is an extended surfactant, $C_{14-15}(PO)_8SO_4Na$, provided by Sasol North America (Lake Charles, LA). An extended surfactant was selected because this type of surfactant is known to exhibit better interactions, i.e. lower interfacial tension and higher solubilization, with polar oils and triglycerides [18]. The surfactant has a methyl-branched alkyl chain of 14 to 15 carbons and approximate eight PO units with average molecular weight of 715 g/mol. The sample used in this work has an active content of 29.6% wt. with 3.8 % free oil (unsulfated alcohol), 0.2% wt. Na_2SO_4 and 66.4% wt. water. The sample was used as received.

***Methods**:* The dynamic interfacial tension (IFT) of oil and surfactant solution was determined using a spinning drop tensiometer (Model 500, University of Texas). The IFT measurements were made using 1-2 μL of oil injected into 300 μL of surfactant solution in a capillary tube. Reported IFT values were recorded at 15 min because IFT values were relatively stable after 10 min. Salinity scans to determine optimum salinity and IFT for each oil were conducted by measuring dynamic IFT of a series of 0.1% wt. solutions of $C_{14,15}(PO)_8SO_4Na$ at various NaCl concentrations. The NaCl concentration at which the minimum IFT* was observed is designated as the optimum salinity (S*). All experiments were conducted at room temperature of $25 \pm 1^{o}C$.

Results and Discussions

Effect of polar ester groups and molecular configuration

Figure 2.1 presents salinity scans of tricaprylin, a short chain synthetic saturated triglyceride (C8:0), hexadecane, a highly hydrophobic *n*-alkane oil, and methyl oleate, a mono-ester of methanol and oleic acid (mono-unsaturated). The results show that although methyl oleate has more carbons (19 carbons) than hexadecane (16 carbons), its optimum salinity (3%) is less than half that of hexadecane (7%). This suggests that the ester group in the methyl oleate molecule reduces its oil hydrophobicity relative to hexadecane. One might suspect that the degree of unsaturation (methyl oleate has one double bond in its hydrocarbon chain) would contribute to the decreased hydrophobicity of methyl oleate. However, results shown later indicate that addition of double bonds in the oil molecule increases the oil hydrophobicity, i.e. requires higher optimum salinity.

The effect of the polar ester groups in oil hydrophobicity can be observed when contrasting the optimum salinity of tricaprylin and hexadecane in Figure 2.1. While the difference in carbon numbers between tricaprylin and hexadecane is large (27 carbons vs. 16 carbons, respectively), the optimum salinity values are virtually the same (7.25% vs. 7%, respectively), indicating that tricaprylin has an EACN of 16 (see Figure 2.1 and Table 2.1). These results demonstrate that although tricaprylin has 70% more carbon atoms than hexadecane, its three ester groups apparently offset the additional carbon atoms and result in an EACN value similar to hexadecane.

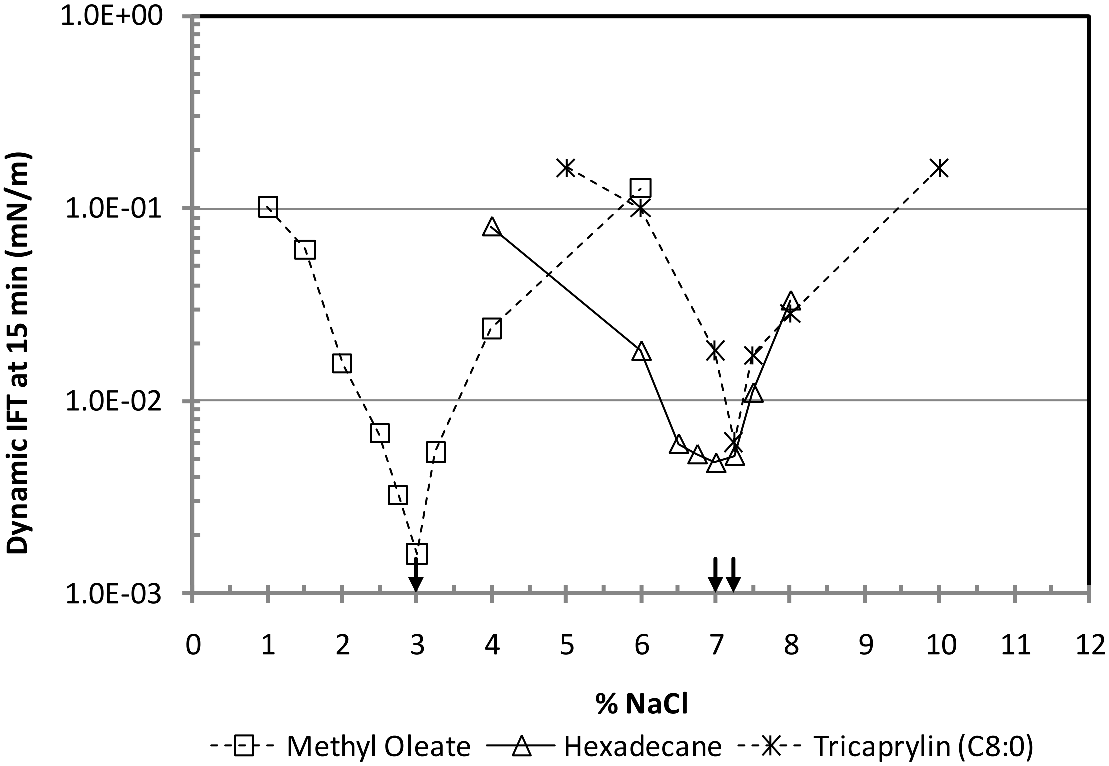

Figure 2.1 Salinity scans of methyl oleate (a mono-ester C18:1), hexadecane and tricaprylin (a short-chain saturated triglyceride C8:0) showing the effect of polar ester group on S* and IFT*. Salinity scans were conducted at 0.1% wt. $C_{14,15}$-$(PO)_8$-sulfate at 25°C. Arrow (↓) points to optimum salinity for each oil.

The reduced oil hydrophobicity due to the polar ester groups observed in this work is in good agreement with the findings of Minana-Perez et al. [10] who concluded that the polar portion of oil molecules considerably decreases the oil EACN. Reduction in oil EACN due to polar ester group was also observed by Queste et al. [22] who reported the EACN of isopropyl myristate (17 carbons with an ester group) to be 7.5 (i.e. less than expected for 18 carbons).

Effect of triglyceride hydrocarbon chain length

Figure 2.2 presents salinity scans of two short-chain saturated triglycerides and three mono-unsaturated triglycerides. For the saturated triglycerides, the optimum salinities of tricaprylin (C8:0) and trinonanoin (C9:0) were approximately the same (7.25% and 7.5% NaCl, respectively) despite a total increase of three carbons in the trinonanoin molecule versus tricaprylin. For the unsaturated triglycerides, the optimum salinities of trimyristolein (C14:1), tripalmitolein (C16:1) and triolein (C18:1) are 9.25%, 10.5% and 11.25% NaCl, respectively. Therefore, an increase of two carbons in each fatty acid chain, i.e. a total of six carbons per triglyceride molecule, resulted in an increase in optimum salinity of approximately 1% NaCl. These increases in the optimum salinities of the triglyceride oils are relatively small when compared to those of *n*-alkane oils, e.g. decane has an optimum salinity of 3.25% NaCl and hexadecane has an optimum salinity of 7% NaCl. Thus, increasing the carbon length of triglycerides increases the optimum salinity required and thus correlates to increasing EACN values. Engelskirchen et al. [13] likewise reported that the EACN of saturated triglycerides increases with increasing alkyl length (C10:0 having an EACN of 13, C16:0 having an EACN of 22).

From Figure 2.2, the change in IFT* values when increasing fatty acid chain length of the studied triglycerides is relatively small. IFT* values of the two saturated triglycerides, tricaprylin (C8:0) and trinonanoin (C9:0), were approximately the same (0.0061 and 0.0041 mN/m, respectively). IFT* values of the mono-unsaturated triglycerides increased from 0.0058 mN/m for trimyristolein (C14:1) to 0.0106 mN/m for triolein (C18:1).

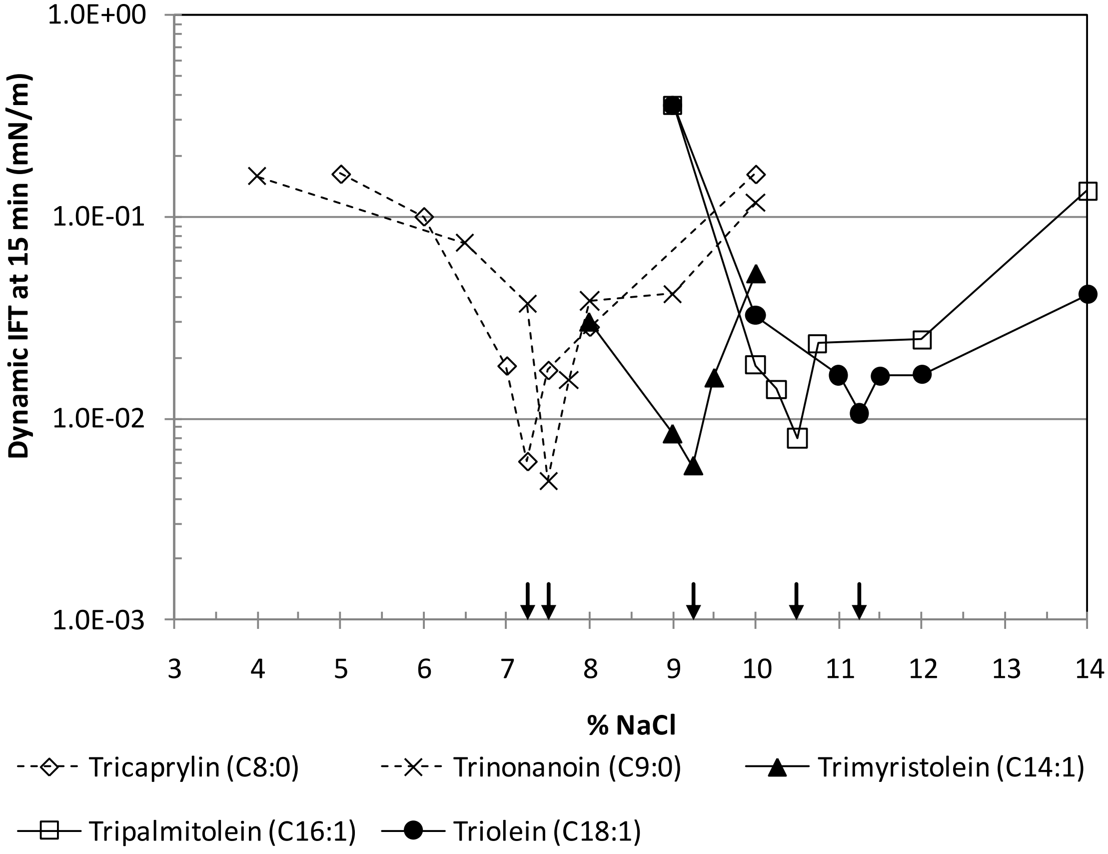

Figure 2.2 Salinity scans of short-chain saturated triglycerides and mono-unsaturated triglycerides showing the effect of chain length variations on S* and IFT*. Salinity scans were conducted at 0.1% wt. $C_{14,\ 15}$-$(PO)_8$-sulfate at 25^{o}C. Arrow (↓) points to optimum salinity for each oil.

Effect of triglyceride degree of unsaturation

Figure 2.3 presents salinity scans of tricaprylin (C8:0) plus three unsaturated triglycerides having the same fatty acid chain length (C18) with increasing number of double bonds in the fatty acid chain. The data show that the C18 triglyceride oils have increasing hydrophobicity with increasing degree of unsaturation (C18:1 versus C18:2 and C18:3). The optimum salinity increased from 11.25% NaCl for triolein (C18:1) to 12.5% for trilinolein (C18:2) and to 14% NaCl for trilinolenin (C18:3).

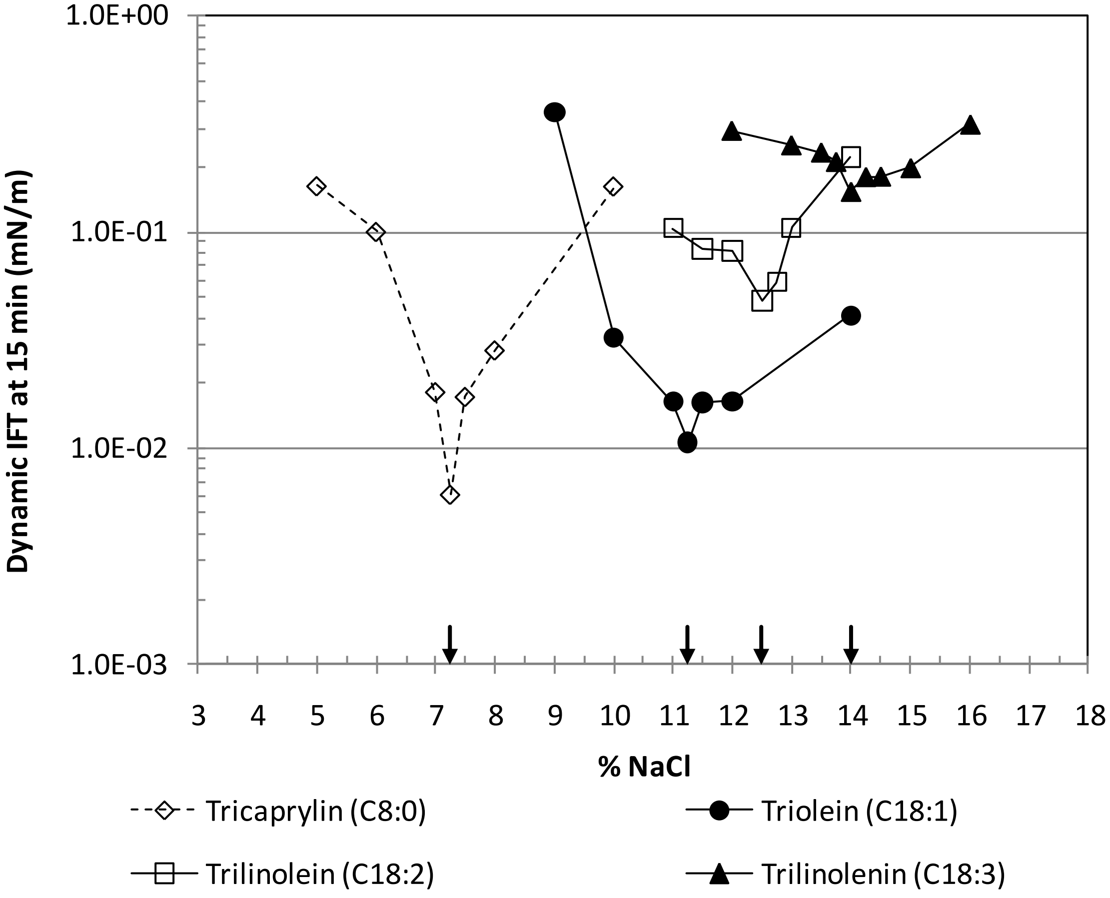

Figure 2.3 Salinity scans of triglycerides showing the effect of degree of unsaturation on S* and IFT*. Salinity scans were conducted at 0.1% wt. $C_{14,\ 15}$-$(PO)_8$-sulfate at 25°C. Arrow (↓) points to optimum salinity for each oil.

From Figure 2.3, the IFT* values are observed to increase significantly when going from C18:1 (triolein) to C18:3 (trilinolenin). The IFT* values increased from 0.0106 mN/m for triolein (C18:1), to 0.0479 mN/m for trilinolein (C18:2), to as high as 0.1538 mN/m for trilinolenin (C18:3). One might expect that the addition of double bonds would make the triglycerides more hydrophilic because of the polarizable nature of the double bonds. However, the increase in optimum salinity with increasing number of double bonds suggests the reverse effect, i.e. triglycerides behave as more hydrophobic (require a higher optimum salinity). We next compared the optimum salinity and IFT* values of a pair of saturated and unsaturated triglycerides with the same fatty acid chain length (C11). The optimum salinity and IFT* values of triundecanoin (C11:0) and tridecenoin (C11:1) both measured at 35°C (triundecanoin is a solid at 25°C) were 7.25 and 8.5% NaCl, and 0.0012 and 0.0078 mN/m, respectively (data not shown). This corroborates the observation that double bonds increase hydrophobicity (requires higher optimum salinity) and increase IFT*. A similar trend was reported by Nardello et al. [20] as they reported EACN values of saturated squalane to be 22.0 vesus unsaturated squalene to be 29.1 obtained from ethoxylated isotridecanol (i-$C_{13}E_n$, n=2-6) systems. Although having the same number of carbon, squalene's double bonds resulted in it being more hydrophobic (higher EACN). However, Engelskirchen et al. [13] (used ethoxylated n-decyltetraoxyethylene $C_{10}E_4$) report the opposite effect for triolein (C18:1, EACN=22) and its saturated counterpart tristearin (C18:0, EACN=25). One potential explanation for the different result for

Engelskirchen's work versus for Nardollo's work and the results in this work could be that the EACN of tristearin is evaluated below its melting point (i.e. supercooled melt in Engelskirchen et al. [13]) which might impact the resulting EACN value.

Table 2.1 Melting point, optimum salinity and EACN of methyl oleate, triglycerides and vegetable oils

Oil	Melting point (^oC)	Optimum salinity (% NaCl)	EACN $_{\text{present work}}$
Methyl Oleate	-19(*)	3.00	9.3
Tricaprylin (C8:0)	10(*)	7.25	16
Trinonanoin (C9-0)	8-9(*)	7.50	16
Trimyristolein (C14:1)	-	9.25	18
Tripalmitolein (C16:1)	-	10.25	19
Triolein (C18:1)	5.5(**)	11.25	19
Trilinolein (C18:2)	-13.1(**)	12.50	20
Trilinolenin (C18:3)	-24.2(**)	14.00	21
Peanut oil	-	10.00	19
Canola oil	-	9.75	18
Olive oil	-	9.75	18

(*) From [25]
(**) From [1]

From Table 2.1, it is noted that the melting points of the triglycerides decrease greatly when degree of unsaturation increases (Triolein: 5.5°C, Trilinolenin: -24.2°C). This indicates a looser packing of the triglyceride oils, or in other words, decreasing interaction energy among triglyceride molecules, with increasing degree of unsaturation. Similarly, the interaction energy between surfactant and triglyceride molecules might decrease with increasing degree of unsaturation, speculatively due to the more complicated (crooked) spatial arrangement of the triglyceride hydrocarbon chain caused by the double bonds. This decreased interaction energy might cause the unsaturated triglycerides behave as more hydrophobic oils (require higher salinity) with increasing degree of unsaturation.

EACN of triglycerides and vegetable oils

The method used to determine EACN values for unknown oils is based on the equation suggested by Salager et al. [17]

$$\ln(S^*) = k(\mathrm{EACN}) + f(A) - \sigma + \alpha_T \Delta T \qquad (2\text{-}2)$$

where S^* is the optimum electrolyte concentration in % wt. NaCl; $f(A)$ is a function of the alcohol used as co-surfactant (absent in this study); σ is a parameter representative of the surfactant; ΔT is the temperature deviation from a reference temperature (at 25^{o}C), and k and α_T are empirical constants.

In this research, salinity scans of different oils were conducted with the same surfactant and concentration, at constant temperature (25^{o}C, $\Delta T=0$), and without alcohol ($f(A)=0$). Therefore, the EACN of each oil is related to its optimum salinity by the simplified equation:

$$\ln(S^*) = k(\mathrm{EACN}) - \sigma \qquad (2\text{-}3)$$

The k and σ parameters for the extended surfactant were determined using linear regression from optimum salinities with *n*-alkanes (hexane, octane, decane, dodecane, tetradecane and hexadecane) as shown in Figure 2.4; by definition, the ACN values of these alkanes are 6, 8, 10, 12, 14 and 16, respectively. Thus, for the surfactant in this study:

$$\ln(S^*) = 0.13 * \text{EACN} - 0.11 \tag{2-4}$$

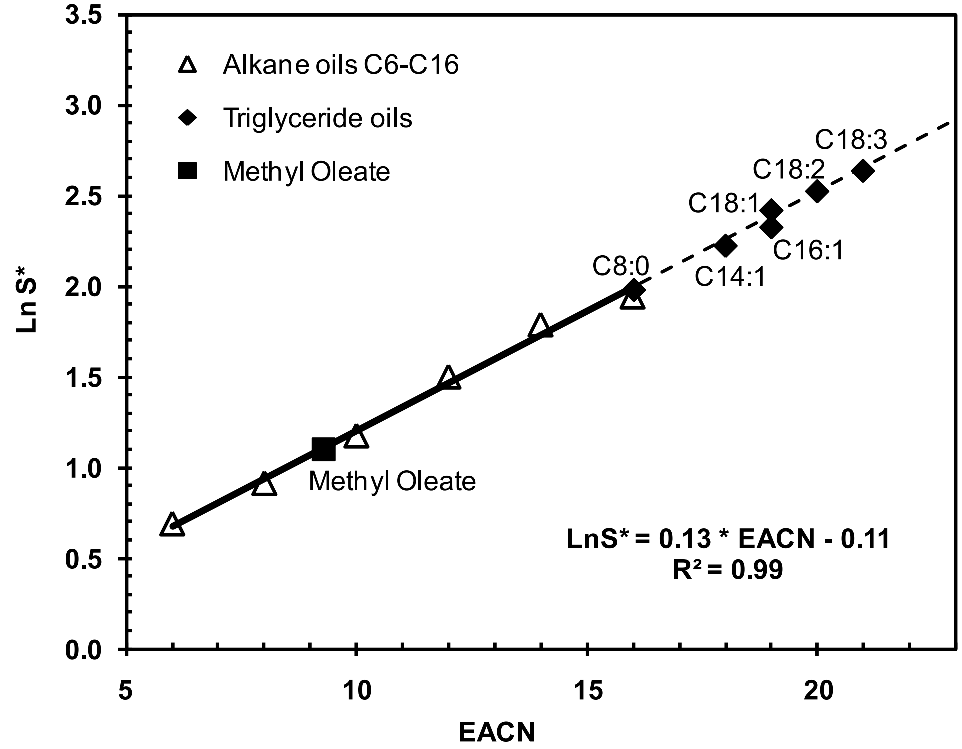

Figure 2.4 LnS* versus EACN of alkane oils (Hexane, Octane, Decane, Dodecane, Tetradecane and Hexadecane), Methyl Oleate and trigyceride oils (Tricaprylin C8:0, Trimyristolein C14:1, Tripalmitolein C16:1, Triolein C18:1, Trilinolein C18:2, Trilinolenin C18:3). Optimum salinity S* was determined by salinity scan of IFT at various NaCl concentrations and 0.1% wt. $C_{14,15}$-$(PO)_8$-sulfate at 25°C.

Eq.2-4 shows a linear correlation of lnS* and ACN of *n*-alkanes with R^2=0.99, which is expected for anionic surfactants [15, 17] as well as for extended surfactant [18, 19, 24]. The k value depends on surfactant types [15] and also number of PO groups in the case of extended surfactant [18]. The k value of 0.13 in this work is close to values reported for an extended surfactant (0.104) [24] and conventional anionic surfactants (0.1-0.16) [15]. Using Eq. 2-4 and the measured optimum salinity values, the EACN of methyl oleate, the studied triglyceride and vegetable oils were estimated as summarized in Table 2.1.

The results show that methyl oleate has an EACN of 9.3, which is comparable to the EACN of 7 reported for ethyl oleate by Minana et al. [18]. As discussed above, tricaprylin has a hydrophobicity similar to hexadecane with an EACN of 16. For unsaturated triglycerides, a four-carbon increase in chain length (C14:1 to C18:1) resulted in one EACN unit increase while the addition of one double bond resulted in approximate one unit increase in EACN. Triolein has an EACN of 19 which reasonably reflects its highly hydrophobic nature. From Table 2.1, EACN values of some common vegetable oils (peanut, canola, and olive) are around 18-19, which are very close to the EACN of triolein, the most abundant component in vegetable oils, and similar to the EACN values reported for vegetable oils (EACN=18-19) by others [18, 24] using different extended surfactants. It is thus seen that the EACN values of high purity triolein reported in this work and Engelskirchen's work are consistent with vegetable oil properties.

Acknowledgements

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CHAPTER 3

Effect of Extended Surfactant Structure to Interfacial Tension and Microemulsion Formation with Triglycerides

Abstract

In this work, the impacts of extended surfactant structure (number of PO groups, length and branching nature of the hydrocarbon chain) on microemulsion formation and IFT values with triglyceride oils were examined. The results show that branching of hydrocarbon tail of extended surfactants lowers optimum salinity, and IFT values as well as enhances triglyceride solubilization through middle phase microemulsion formation. The results also show that ultralow IFTs with vegetable oils can be achieved using extended surfactants with eight polypropylene oxide (PO) groups or more.

Key words: triglycerides, vegetable oils, microemulsion, extended surfactant, solubilization, interfacial tension

Introduction

Triglycerides are the main components in vegetable oils, fish oils and algae oils. Traditionally, triglycerides have been used as important lipid sources in human diet and for cooking purposes [1]. Recently, triglycerides have been explored as environmental friendly and renewable materials in industrial processes and as natural ingredients in consumer products [2-6]. Microemulsions have many unique characteristics that can be exploited in new triglyceride applications. For example, triglyceride microemulsions can achieve low interfacial tension (IFT) which is essential in applications like oil and grease detergency or water-based extraction of triglycerides from oil seeds or algae. Other microemulsion characteristics, such as thermo-dynamical stability, transparency and high solubilization capacity, are the required properties in applications such as biodiesel, cosmetic and pharmaceutical products. Therefore, triglyceride microemulsions are of special research interest.

Microemulsions are thermodynamically stable mixtures of oil and water produced using surfactant formulations [7]. Microemulsions have been thoroughly reviewed elsewhere [7-10]. In short, microemulsion systems can be classified into three categories known as Winsor Type I, II, III microemulsions. In Winsor Type I microemulsions, the oil is solubilized in normal micelles in the water phase. In Winsor Type II microemulsions, water is solubilized in reverse micelles in the oil phase. Winsor Type III microemulsions sometimes referred to as middle phase microemulsions, can be envisioned as both water and oil swollen micelles in a bi-continuous structure [7]. With increasing hydrophobicity of the surfactant system (e.g. increasing salinity for anionic surfactant system), the microemulsion system transitions from Winsor Type I, to Type III and to Type II (Figure 3.1) and the oil/water interfacial tension $IFT_{o/w}$ goes through a minimum value at optimum condition in Winsor Type III region. Salinity, IFT and solubilization parameter (volume of oil or water solubilized in microemulsion per mass of surfactant) at optimum conditions are denoted as S*, IFT* and SP*.

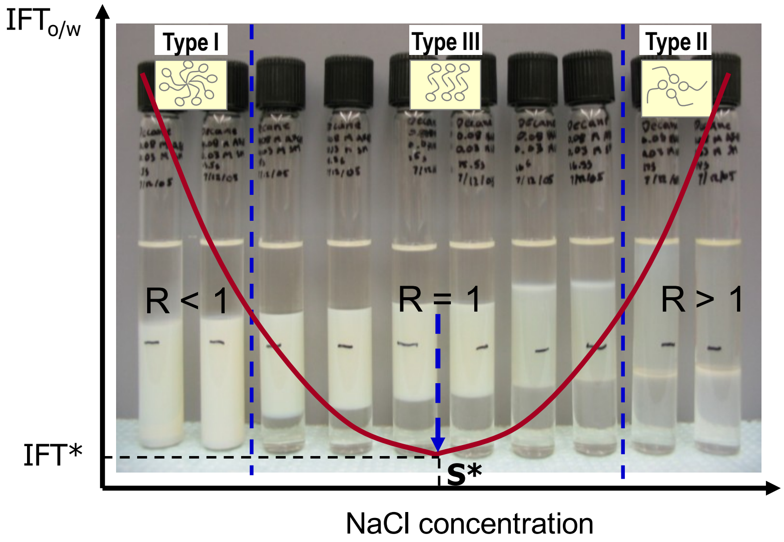


Figure 3.1 Typical microemulsion phase transition and IFT$_{o/w}$ profile in a salinity scan of an anionic surfactant system

Despite extensive microemulsion work with *n*-alkane oils or chlorinated hydrocarbons, triglycerides remain the most challenging oil to microemulsify due to their unique structures. Triglycerides are esters of glycerol and three fatty acids, which may have the same or different alkyl lengths and can be saturated or unsaturated. The hydrocarbon chains of the fatty acids can be as long as 24 carbons and are non-branched [6]. Several researchers have reported triglyceride microemulsion formation using different approaches such as co-oil addition, alcohol addition, non-ionic surfactants at high temperature, and extended surfactants with linkers [11-21]. Among the published work on triglyceride microemulsions, the use of extended surfactant in triglyceride microemulsion [14, 20-23] has gained special interest because of the ability of extended surfactants to provide ultralow IFT and very high solubilization enhancement.

Extended surfactants were first introduced in 1995 by Minana-Perez et al [14]. The concept of extended surfactants (Figure 3.2) originated from the effort to try to increase the surfactant-oil interaction. Attempting to increase this interaction by increasing surfactant hydrocarbon chain length is limited to 18 carbons due to surfactant precipitation beyond that point. To overcome this limitation, polypropyleneoxide (PO) groups, which have intermediate polarity, were inserted between the head group and the tail of the surfactant. The introduction of PO groups in the hydrophobe of the surfactant molecules helps to extend the tail further into the oil phase without sacrificing water solubility due to the longer tail. On the water side, the interactions with the water phase can be enhanced by inserting polyethyleneoxide (EO) groups. This arrangement is also believed to provide a smoother transition in polarity at the interface [7] which is considered a key factor in achieving high solubilization with highly hydrophobic oils (e.g. long chain hydrocarbons and triglycerides). Although previous work has demonstrated that extended surfactants can provide ultralow IFT and high solubilization capacity for triglyceride microemulsions [7, 14], limited information is available on how the structure of extended surfactant molecules affect their IFT values and their ability to form microemulsions with different triglyceride oils.

This work evaluates the impact of extended surfactant structure (e.g. number of PO groups, length and branching nature of the hydrocarbon chain) on microemulsion phase behavior and IFT values with triglyceride oils. Understanding these effects is of great importance for optimizing extended surfactant structures to deliver desired microemulsion properties for various triglyceride applications.

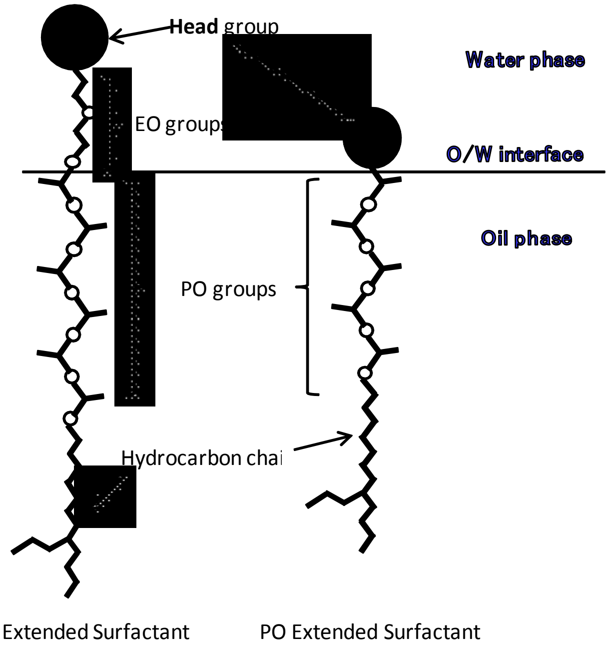


Figure 3.2 Schematic of extended surfactant molecule configuration

Materials and Methods

Materials Two categories of extended surfactants were used in this work. The first category is sodium alkyl polypropylene oxide sulfate surfactants (R–$(PO)_x$–SO_4Na) provided by Sasol North American Inc. (Lake Charles, LA). The second category is sodium linear-alkyl polypropoxylated polyethoxylated sulfate surfactants (R–(PO)z–

$(EO)_2$–SO_4Na) provided by Huntsman Petrochemical Corp (Houston, TX). Properties of the surfactants are summarized in Table 3.1. All extended surfactants were used as received.

Table 3.1 Properties of extended surfactants

Nomenclature	Chemical Formula	Degree of branching (%)	% active	Molecular weight (g/mol)
C123(B)-4PO-SO_4(*)	$C_{12,13}H_{25,27}$-$(PO)_4$-SO_4Na	100	30.0	527
C123(B)-8PO-SO_4	$C_{12,13}H_{25,27}$-$(PO)_8$-SO_4Na	100	30.7	766
C145(B)-4PO-SO_4	$C_{14,15}H_{29,31}$-$(PO)_4$-SO_4Na	100	30.0	553
C145(B)-8PO-SO_4	$C_{14,15}H_{29,31}$-$(PO)_8$-SO_4Na	100	29.5	783
C123(L)-4PO-SO_4	$C_{12,13}H_{25,27}$-$(PO)_4$-SO_4Na	100	27.3	519
C123(L-B)B-4PO-SO_4	$C_{12,13}H_{25,27}$-$(PO)_4$-SO_4Na	50	28.1	527
C12(L)-14PO-2EO-SO_4	$C_{12}H_{25}$-$(PO)_{14}$-$(EO)_2$-SO_4Na	0	24.7	1104
C12(L)-18PO-2EO-SO_4	$C_{12}H_{25}$-$(PO)_{18}$-$(EO)_2$-SO_4Na	0	23.8	1265

(*) Cxyz refers to alkyl length in mixture (C123 indicates C12/13 mixture)
B indicates 100% branched hydrocarbon chain; L indicates 100% linear hydrocarbon chain
L-B indicates 50% linear-50% branched hydrocarbon chain
aPO indicates number of PO groups; bEO indicates number of EO groups

Tricaprylin and canola oil were used in this work to represent short chain saturated triglycerides and long chain unsaturated triglycerides, respectively. Hexadecane, a highly hydrophobic *n*-alkane, was also used to evaluate the effects of branching of 4-PO extended surfactants. Tricaprylin and hexadecane with 99% purity were purchased from Sigma Chemicals (St. Louis, MO). Canola oil was purchased from a local store. Sodium chloride (> 99% purity) was purchased from Sigma-Aldrich (St. Louis, MO).

Methods

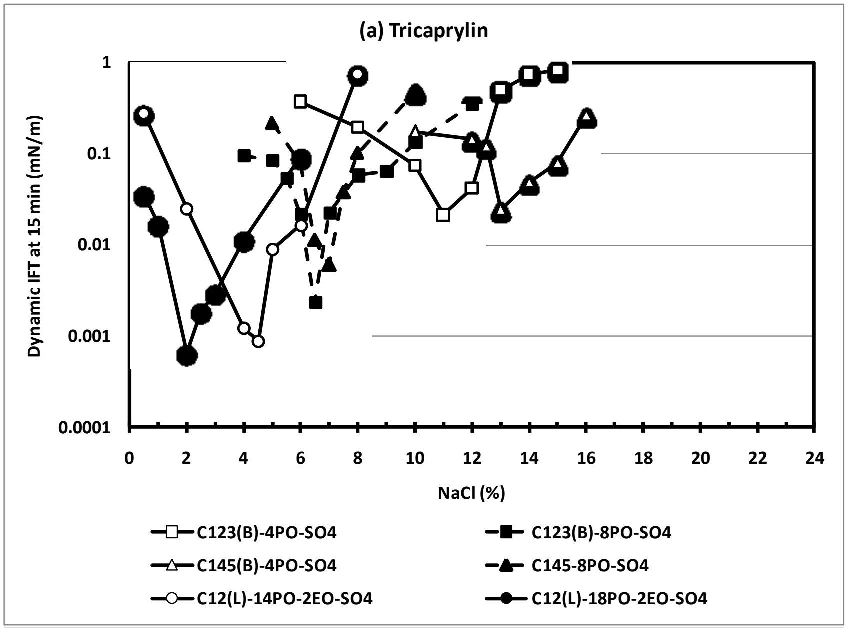
Phase behavior studies were conducted using salinity (NaCl) scans at different surfactant concentrations at an oil to water ratio of 1:1 and surfactant concentration of 0.08M. The samples were kept at room temperature of 25 ± 1°C and were gently shaken once per day for three consecutive days and then left undisturbed for two weeks to reach equilibrium before assessing microemulsion phases.

The dynamic interfacial tension (IFT) of oil and surfactant solution was determined using a spinning drop tensiometer (Model 500, University of Texas). The IFT measurements were made using 1-2 μL of oil injected into 300 μL of surfactant solution in a capillary tube. Reported IFT values were recorded at 15 min after oil injection.

Results and Discussions

Effect of PO groups on dynamic IFTs

Figure 3.3 presents the dynamic IFT values of six extended surfactants with tricaprylin and canola oil. It is noted that there are three pairs of extended surfactants having the same hydrocarbon chain but with different number of PO groups: C123(B)-4PO-SO_4Na vs. C123(B)-8PO-SO_4Na, C145(B)-4PO-SO_4Na vs. C145(B)-8PO-SO_4Na and C12(L)-14PO-2EO-SO_4Na vs. C12(L)-18PO-2EO-SO_4Na. This setup allows us to evaluate the effect of PO groups on IFT values. The results showed that when the number of PO groups in the extended surfactants increase, both optimum salinity and minimum IFT values decrease. The decreased optimum salinities with increasing number of PO groups are expected because PO groups have been reported to be part of the hydrophobic tail of the surfactants [13]. What is of interest in this work is the relationship between number of PO groups and the ability to achieve ultralow IFT (< 0.1 mN/m) with triglyceride oils. The results show that for the short-chain saturated triglyceride tricaprylin C8:0 (EACN=16, [22]), all the studied extended surfactants (PO ≥ 4) were able to achieve ultralow (<< 0.1 mN/m). However, for canola oil (EACN=18, [22]), the 4-PO extended surfactants could not achieve ultralow IFT (IFT* values were in the range of 0.2-0.5 mN/m). In contrast, the 8-PO and xPO-2EO extended surfactants were able to achieve IFT values much less than 0.1 mN/m for the canola oil. While we are not aware of triglyceride IFT data for 4-PO extended surfactants in the literature, the IFT values of the 8-PO and 18PO-2EO extended surfactants in this work are in good agreement with IFT values reported for triolein and vegetable oils for the same types of extended surfactant [20-21]. It is noted that IFT values of the xPO-2EO extended surfactants are consistently lower than those of to the 8-PO extended surfactants by as much as an order of magnitude. The lower IFT and optimum salinity values suggests that the xPO-2EO extended surfactants have stronger interactions with the oils (and water) compared to the 8-PO extended surfactants. However, it is not clear whether the increase in number of PO groups or the presence of two EO groups (or both) is responsible for this effect.


(a) Tricaprylin

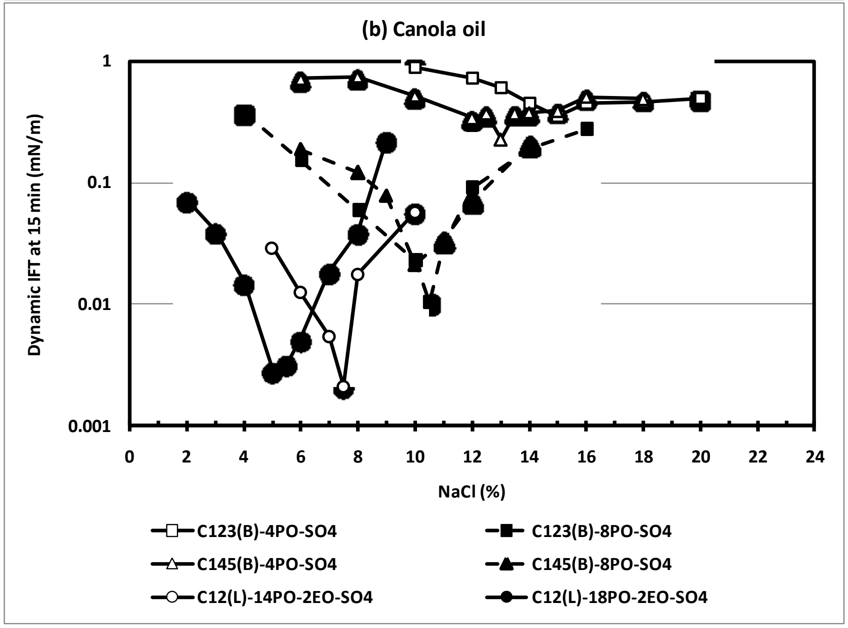
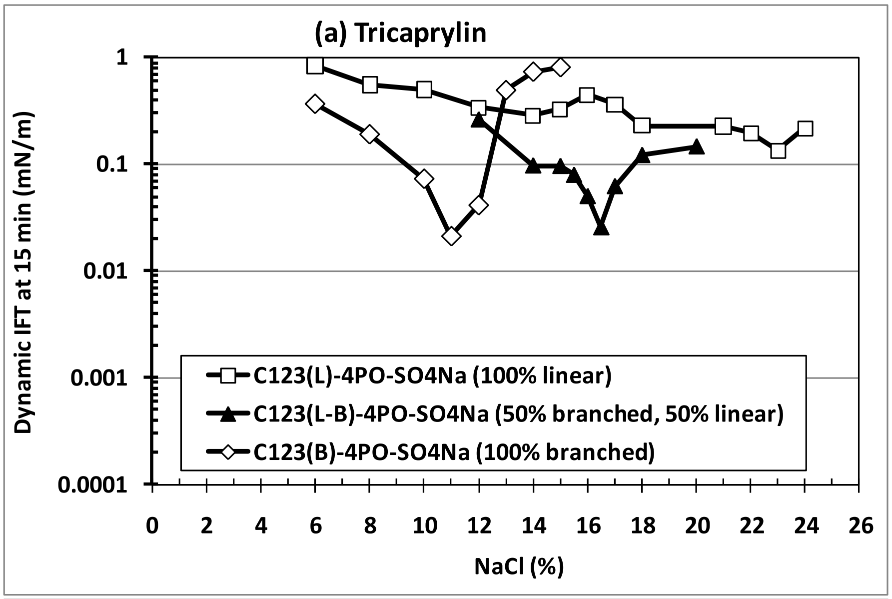

(b) Canola oil

Figure 3.3 Salinity scans of extended surfactants and tricaprylin and canola oil showing the effect of PO groups on S* and IFT*. Salinity scans were conducted at 0.1% wt. surfactant concentration at 25^{o}C

Effect of hydrocarbon branching on IFTs

Figure 3.4 presents dynamic IFT values of a series of three extended surfactants with tricaprylin and hexadecane. Because the 4-PO extended surfactants could not achieve ultralow IFT with canola oil, hexadecane was selected to study the effect of branching in addition to tricaprilin. The three surfactants all have four PO groups but the structures of the hydrocarbon chain are different. The hydrocarbon chain of the C123(B)-4PO-SO_4Na surfactant is a mixture of monobranched alkyl of C12 and C13 (100% branched). The hydrocarbon chain of the C123(L)-4PO-SO_4Na surfactant is a mixture of linear alkyl of C12 and C13 (100% linear). The hydrocarbon chain of the C123(L-B)-4PO-SO_4Na surfactant is a mixture of monobranched alkyl of C12 and C13 and linear akkyl of C12 and C13 (50% branched, 50% linear). The results show that the optimum salinity decreased dramatically with increasing degree of branching in the hydrocarbon tail. For tricaprylin, the optimum salinity (S*) is 23% NaCl for C123(L)-4PO-SO_4Na while it is 11% NaCl for C123(B)-4PO-SO_4Na. The same trend of decreasing optimum salinity with increasing branching was observed for hexadecane. The degree of branching also impacts the IFT values for tricaprylin, i.e. only the branched surfactants (C123(B)-4PO-SO_4Na and C123(L-B)-4PO-SO_4Na) can achieve ultralow IFT (<0.1 mN/m) while the linear surfactant C123(L)-4PO-SO_4Na has an IFT value of 0.13 mN/m. However, interestingly enough degree of branching had little effect on the IFT values of hexadecane (all < 0.01 mN/m) even though it did impact the optimum salinity.



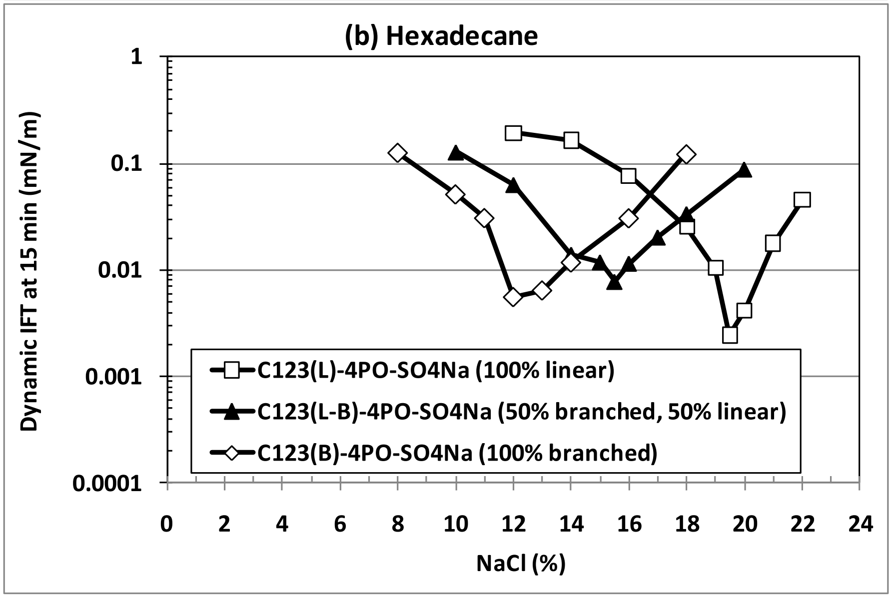


Figure 3.4 Salinity scans of extended surfactants and tricaprylin and hexadecane showing the effect of surfactant hydrocarbon tail branching on S* and IFT*. Salinity scans were conducted at 0.1% wt. surfactant concentration at 25^{o}C

Only limited work has evaluated on the impact of branching on the performance of extended surfactants. Aoudia (1995) [23] reported that the optimum salinity of twin-tailed extended surfactants is less sensitive in comparison to methyl branched extended surfactants with *n*-alkanes. Based on these observations, we speculate that the branched hydrocarbon reduces the tail-tail interactions between extended surfactants which have quite long tails due to the PO groups. Therefore, the interactions between surfactant and oil molecules are more favorable, leading to the decrease in optimum salinity and IFT values when the degree of branching increases in the surfactant tail.

Effect of extended surfactant structure on triglyceride microemulsion formation

Table 3.2 summarizes the results of triglyceride phase behavior studies of selected extended surfactants with different hydrocarbon chain length, branching degree and number of PO groups. Optimum salinity and IFT values were obtained from dynamic IFT scans (i.e. oil injected into IFT device rather than pre-equilibrated with oil in phase behavior studies). For the 4-PO extended surfactants, no microemulsion was observed with canola oil and only Winsor Type I and II microemulsions were observed with tricaprylin. At the salinities where Winsor Type III is expected, a sponge phase was observed, i.e. the surfactants separate out from the water phase and concentrate at the oil interface but no oil was solubilized into this surfactant phase. The 8-PO extended surfactants were able to form Winsor Type I, III and II with both canola oil and tricaprylin. These observations were expected because these surfactants can achieve ultralow IFTs with both canola oil and tricaprylin. The solubilization parameters (SP*) for tricaprylin (5.5-6.0 mL/g) are significantly higher than those of canola oil (3.3-3.4 mL/g), but lower than values reported by Minana-Perez et al (20 mL/g) [14] using extended surfactant systems without additives at 35°C. However, these values are comparable to values reported by Do et al (6-10 mL/g for vegetable oils) [21] using extended surfactants and a combination of hydrophilic/lipophilic linkers.

Surprisingly, the PO-EO surfactants, which have ultralow IFT values with both canola oil and tricaprylin, could not form Winsor Type III even though Winsor Type I and II were observed. Instead, sponge phase is observed where middle phase microemulsion is expected. The sponge phase has also been reported by others [13, 21] in their work with triglyceride microemulsions. This observation deviates from the Chun-Huh relationship [24] which predicts high solubilization (i.e. middle phase microemulsion) when ultralow IFT is achieved. Whereas IFT reduction is related to surfactant adsorption at the interface and thus the magnitude of surfactant-oil-water interaction, microemulsion formation is related to solubilization of oil (or water) into surfactant aggregates. Therefore, polar and bulky molecules like triglyceride molecules need surfactant aggregates large enough and with a desirable environment to accommodate these molecules.

Table 3.2 Microemulsion phase behavior of extended surfactants and triglyceride oils

Surfactant	**Canola oil**				**Tricaprylin**			
	S* (% NaCl)	**IFT* (mN/m)**	**SP*[(1)] (mL/g)**	**Phase Behavior**	**S* (% NaCl)**	**IFT* (mN/m)**	**SP*[(1)] (mL/g)**	**Phase Behavior**
C123(B)-4PO-SO_4	15.0	0.4547	-	No microemulsion observed	11.0	0.0213	-	Type I, sponge[(2)], II
C145(B)-4PO-SO_4	13.0	0.2268	-	No microemulsion observed	10.5	0.0244	-	Type I, sponge, II
C123(B)-8PO-SO_4	10.5	0.0104	3.3	Type I, III, II	7.0	0.0011	5.5	Type I, III, II
C145(B)-8PO-SO_4	10.0	0.0214	3.4	Type I, III, II	7.0	0.0060	6.0	Type I, III, II
C12(L)-14PO-2EO-SO_4	7.5	0.0104	-	Type I, sponge, II	4.5	0.0009	-	Type I, sponge, II
C12(L)-18PO-2EO-SO_4	5.5	0.0029	-	Type I, sponge, II	2.0	0.0007	-	Type I, sponge, II

(1) SP* = mL of oil (or water) in middle phase per g of surfactant

(2) Sponge phase = the surfactant separates out from the water phase and concentrates at the oil interface but no oil was solubilized into this separate surfactant phase

It is also noted that the 4-PO extended surfactants (branched) and the PO-EO extended surfactants can form Winsor Type I and II with canola oil and tricaprylin (excluding the 4-PO extended surfactants) but not Winsor Type III. Recall that in Winsor Type II microemulsion, water is solubilized in reverse micelles. Therefore, as long as the surfactants have strong enough interactions with the triglyceride oil phase and hydrophobic enough to form reversed micelles, Winsor Type II microemulsion can be formed.

For polar oils like triglycerides, the locus of solubilization is at the palisade layer [10]. Kleven (1950) [25] reported that with increasing electrolyte concentration in ionic surfactant solution, solubilization of polar compounds decreased due to the closer packing of the surfactant molecules (reduced palisade layer). The packing in Winsor Type I region (less electrolyte) is not as close as in Winsor Type III region. This might be the reason why no Winsor Type III microemulsion was observed for the PO-EO surfactants with linear hydrocarbon chains that have strong tail-tail interactions (close packing). This can also explain why the 8-PO surfactants are able to form Winsor Type III microemulsions with canola oil and tricaprylin. The 8-PO surfactants have 100% branched hydrocarbon chain which are expected to have a looser packing density in Winsor Type III region. In summary, with increasing number of PO groups (≥ 8) and branching of the tail of extended surfactants they are able to achieve high solubilization with triglyceride oils, indicating the importance of these parameters when designing surfactant-based solubilization systems.

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CHAPTER 4

Microemulsion-based Vegetable Oil Detergency using Extended Surfactant[*]

Abstract

This work examined the use of a single extended surfactant in microemulsion-based detergency of vegetable oils. The results showed that good canola oil detergency (>80%) was achieved at 25^{o}C using a single extended surfactant ($C_{14,15}$-8PO-SO_4Na) at concentrations as low as 125 ppm. The results also showed that maximum detergency (95%) was achieved in the Type II microemulsion region. These results demonstrate that a microemulsion-based extended surfactant formulation is a highly viable approach for vegetable oil detergency at room temperature, an encouraging step toward "green" detergent products using low surfactant concentrations and reduced wash temperature.

Key words: detergency, vegetable oil, extended surfactant, microemulsion, triglyceride

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Introduction

Surfactant-based fabric detergency of oily soil is a complicated process which has been studied for many years [1-2]. Surfactants have been shown to enhance detergency by lowering the interfacial tension (IFT) between the fabric and the wash solution and the oil and the wash solution since these IFT reductions lower the work required to remove the oil from the fabrics through roll-back or snap-off mechanisms [2-4]. For highly hydrophobic oily soils, such as motor oils or vegetable oils, formulating surfactant systems to achieve low IFT is a challenge. The unique properties of microemulsions have been applied to detergency formulations to take advantage of the ultralow IFT and high solubilization capacity of these microemulsion systems [5-13]. In addition, microemulsion-based detergency is a prospective approach for cold water detergency, a future trend for energy saving detergency formulations [4], as microemulsion systems can be optimized to perform well at lower temperatures.

Triglycerides, the main components in vegetable oils, are very hydrophobic oils that also have a polar nature due to the unique structure of a bulky glycerol group and three long hydrocarbon chains. The combined hydrophobic and polar nature of vegetable oils together with their bulkiness makes them among the most difficult oily soils to remove from fabrics. The commercial approach for vegetable oil detergency is to use high alkalinity or enzymes to hydrolyze the triglycerides and fatty esters to free fatty acids which are more easily removed [4]. Earlier work on triglyceride detergency used non-ionic surfactants [7, 8] and found that good detergency required high temperature (~60^{o}C) and sufficient surfactant concentrations (500-1000 ppm). Recent technical grade triolein work by Tongcumpou et al (2006) [12] showed >80% oil removal using a mixture of anionic and non-ionic surfactants with total surfactant active content of 2500 ppm.

Triglyceride microemulsions [14-20] produce ultralow IFT with triglyceride oils, making microemulsion-based systems an attractive alternative for vegetable oil detergency. Among the published work on triglyceride microemulsions, the use of extended surfactant [21] in triglyceride microemulsion was first reported by Minana-Perez et al. (1995) [16] and followed by others [22-23], demonstrating that ultralow IFT and high solubilization at room temperature are possible. However, to our knowledge no work has been published regarding the use of extended surfactant in vegetable oil detergency. Therefore, extended surfactant formulations optimized for vegetable oil detergency are of special interest. In this work, detergency formulations using a single extended surfactant are evaluated at different salinities and surfactant concentrations to determine formulations that can provide good detergency with vegetable oil at low temperature and low surfactant concentration.

Experimental Procedures

Materials The surfactant used in this work is an extended surfactant $C_{14,15}$-8PO-SO_4Na provided by Sasol North America (Lake Charles, LA). The surfactant has a sulfate head group and a hydrophobic tail of a methyl-branched alkyl of 14 to 15 carbons with approximate eight propylene oxide (PO) units. The sample used in this work has an average molecular weight of 716 g/mol and an active content of 29.5% wt. with 3.8 % free oil (unsulfated alcohol), 0.75% wt. Na_2SO_4 and 65.95% wt. water. The sample was used as received.

Canola oil (Crisco) was purchased from a local store. Sodium chloride (>99% purity) and oil-soluble dye Oil-red-O were purchased from Sigma-Aldrich (St. Louis, MO). All the chemicals were used as received without further purification. Fabric used for detergency testing was white fabric of polyester/cotton (65:35) blend purchased from a local store. Tide cold water (Procter and Gamble Co.) was purchased from a local store and was tested as a representative commercial liquid detergent [10].

Methods Phase behavior studies were conducted using salinity (NaCl) scans at different surfactant concentrations at an oil to water ratio of 1:1 [9, 16, 23]. The samples were kept at room temperature of $25 \pm 1^{o}C$ and were gently shaken once per day for three consecutive days and then left undisturbed for two weeks to reach equilibrium before assessing microemulsion phases [9, 16, 23].

The dynamic interfacial tension (IFT) of oil and surfactant solution was determined using a spinning drop tensiometer (Model 500, University of Texas). The IFT measurements were made using 1-2 μL of oil injected into 300 μL of surfactant solution in a capillary tube [22-23]. Reported IFT values were recorded at 20 min after oil injection.

Detergency testing was conducted in accordance to the procedures described in Tongcumpou et al [10], summarized as follows: 3x4-inch swatches of the test fabric were soiled by submerging completely for 1 min in the canola oil dyed with oil soluble dye Oil-red-O. The soiled fabric was allowed to equilibrate overnight prior to use. The resulting swatches had an average oil content of 0.20 ± 0.03 g per swatch. Detergency experiments were conducted using a Tergi-O-Tometer (Model 7243; USA Testing Co., Inc., Hoboken, NJ). Three prewash soiled swatches (triplicate samples) were washed for 20 min with 1 L of the washing solutions. The wash was followed by two rinse cycles of 3 and 2 min, respectively, with 1 L of deionized water each. All washing and rinse steps were conducted at an agitation speed of 120 rpm and 25 ± 1^{o}C. The postwash swatches were allowed to dry overnight at room temperature prior to determining the detergency efficiency, which was based on the reflectance of the prewash and postwash swatches at 520 nm using the Ultra Scan Sphere Spectrophotometer (Hunter Lab). The detergency (in %) was calculated by the following equation:

$$\text{Detergency } (\%) = [(A - B)/(C_o - B)] \times 100 \qquad (4\text{-}1)$$

where A is the average reflectance of the soiled swatches after washing, B is the average reflectance of the soiled swatches before washing, and C_o is the average reflectance of the unsoiled swatches before washing.

Results and Discussions

Microemulsion Phase Behavior Studies

Figure 4.1 presents the microemulsion phase behavior (fish diagram) of canola oil and the extended surfactant $C_{14,15}$-8PO-SO_4Na. Winsor Type I, III and II systems were observed over a wide range of surfactant concentrations and salinities. Since it is impractical for detergency application, phase behavior studies were not conducted at higher surfactant concentrations (>12.5 % wt.) where Winsor Type IV microemulsion (i.e. Winsor Type III with enough surfactant to solubilize all the oil and water into one phase) would be expected. At low surfactant concentration (low end of the fish diagram), middle phase (Type III) microemulsions were visually observed at surfactant concentrations as low as 0.39 % wt.

Extended-surfactant based vegetable oil microemulsions were first reported in 1995 by Prof. Salager's group [16] at 30^{o}C. We have extended that work by reporting phase diagrams and IFT values in this work, which uses a single surfactant system, as well as in previous studies [22-23] which used combinations of extended surfactant and linker molecules. Other research has used different approaches such as co-oil/alcohol addition, and non-ionic surfactants at high temperature (PIT~50^{o}C) [17-20]. Relative to these previous studies, the current observation of three types of microemulsions with canola oil at room temperature (25 ± 1^{o}C) using a single extended surfactant $C_{14,15}$-8PO-SO_4Na without other additives suggests that this surfactant is a good candidate for room temperature water vegetable oil detergency, and also suggests it as a good candidate for cold water detergency.

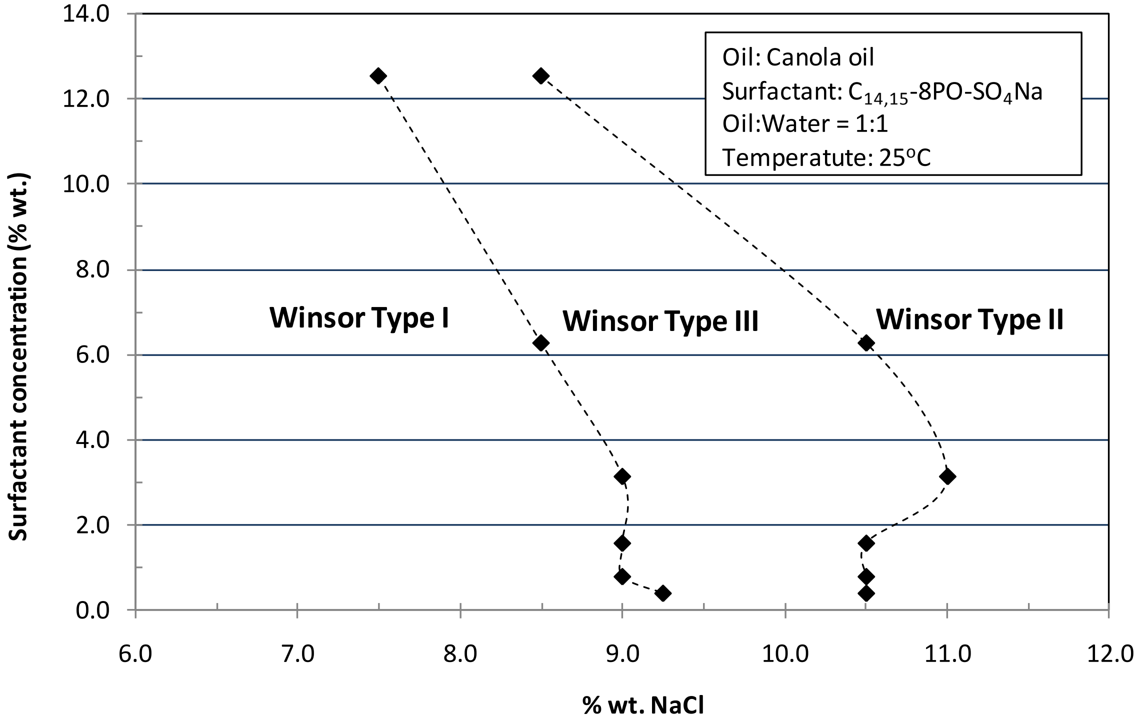


Figure 4.1 Fish diagram of $C_{14,15}$-8PO-SO_4Na/brine/Canola oil microemulsions at 25°C

Detergency vs. salinity

Figure 4.2 presents dynamic IFT values of the wash solutions with $C_{14,15}$-8PO-SO_4Na concentration of 1000 ppm at various NaCl concentrations. With the exception of the wash solution without NaCl (IFT=2.2 mN/m), all other formulations showed wash solution-canola oil IFT values well below 1.0 mN/m (IFT=0.0091 to 0.30 mN/m) for a wide range of salinities (from 2 to 16% NaCl). These IFT values with canola oil are similar to reported values using different extended surfactants [22-23]. These values are significantly lower than the IFT of the commercial liquid detergent product (1.9 mN/m) used in this work at the same surfactant concentration of 1000 ppm. The salinity scan showed that the IFT values at 8, 10 and 12% NaCl are lower (0.0091-0.26 mN/m) compared to the rest of IFT values (0.30-2.2 mN/m), with the minimum IFT value of 0.0091 mN/m recorded at 10% NaCl. Based on the ultralow IFT values, the wash solutions at these three salinities are considered as Type III formulations with the optimum condition being at 10% NaCl. The wash solutions at the salinities from 0 – 6 % NaCl are considered as Type I formulations and those at the salinities of 14% and 16 % NaCl as Type II formulations.

Figure 4.2 also presents the results of the detergency tests using these same wash solutions. In order to examine the relationship between wash solution phase behavior and detergency mechanism in each step of the detergency procedure, two separate sets of detergency tests were performed. The first set was performed with full cleaning procedure including 20-min wash cycle, followed by a 3-min rinse cycle and a 2-min rinse cycle. The second set underwent only the wash cycle without any rinse cycle allowing us to see how much of the cleaning occurred in this first step [11-13]. Detergency achieved by the commercial liquid detergent product and de-ionized water are also presented in Figure 4.2 for comparison.

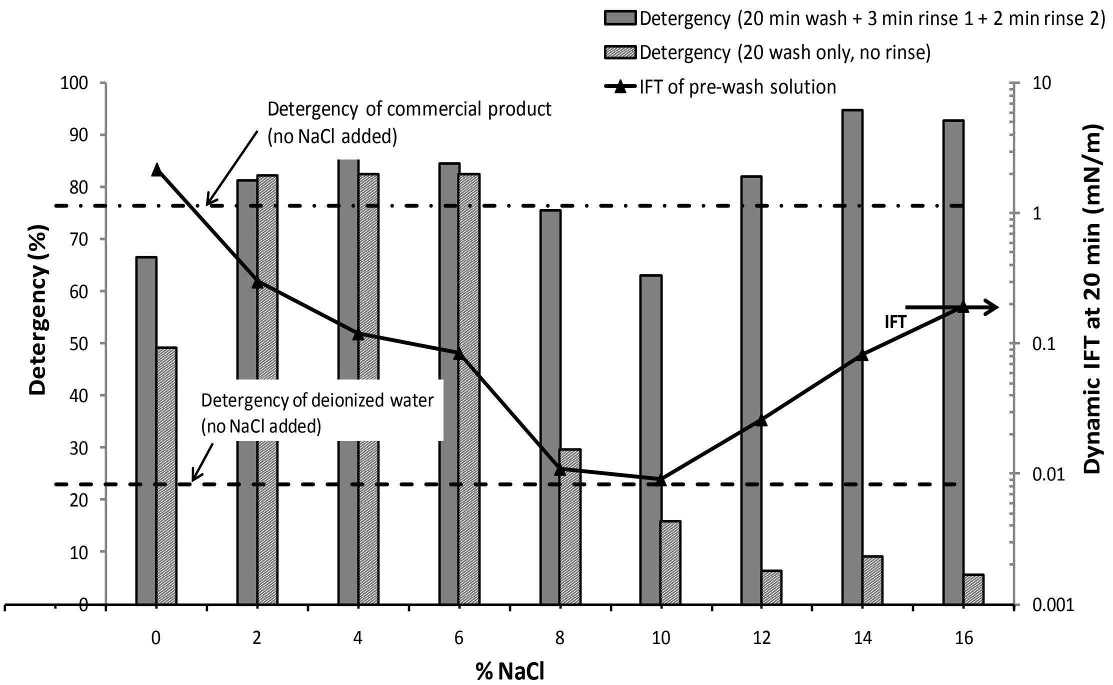


Figure 4.2 Dynamic IFTs (at 20 min) of the wash solutions with canola oil and detergency efficiencies of full procedure test (20-min wash cycle, 3-min rinse-1 cycle and 2-min rinse-2 cycle) and wash only test (20 min wash). Agitation at 120-rpm, temperature at 25°C, 1,000 ppm C14,15-8PO-SO4Na. Commercial product also at 1,000 ppm surfactant active.

Detergency performance obtained by the wash-only set of detergency tests (Figure 4.2) provides insights into detergency mechanisms in each microemulsion region. In the Winsor Type I region (at 2%, 4%, and 6% NaCl), more than 95% of total detergency in the full cleaning procedure was achieved in the wash cycle. The detergency efficiency achieved during the wash cycle decreased dramatically when the wash solution entered the Winsor Type III region, with only 39% and 26% detergency realized in the wash cycle at 8% and 10% NaCl, respectively. The detergency efficiency by the wash cycle was extremely low (less than 10% of total detergency efficiency) when the formulation passed the optimum salinity (Winsor Type III at 12% NaCl and Winsor Type II at 14% and 16% NaCl). Interestingly enough, when the formulations were at the optimum salinity and beyond, the detergency efficiencies in the wash cycle are even lower than the value achieved with only de-ionized water. These results revealed that most of the detergency efficiency of the formulations in the Winsor Type III and Type II regions reported for the wash and rinse cycles occurred during the rinse cycles.

While the detergency efficiencies in the Winsor Type I region can be explained by the well-established roll-back and/or snap-off mechanisms [2-4] as the detergency efficiencies are somehow related to the IFT values of the wash solutions, the oil removal mechanism in Type III and Type II is less clear. Previous work [10-13] has also observed the oil removal during rinse steps beyond that realized in the wash step. The authors explained that the spreading effect [8, 12] caused by ultralow IFTs counteracted oil removal through roll-back and snap-off mechanisms in the wash cycle and the oil was removed in the rinse cycles due to the increase in IFTs during rinsing which made the oil become non-wetting and thus removed by mechanical agitation. While the spreading effect due to low IFTs could be used to explain the detergency observed in the Winsor Type III region in the current work, it cannot explain the poor detergency (realized in the wash step) in the Winsor Type II region as the IFTs were approximately the same as the IFTs in the Winsor Type I region. From a microemulsion phase behavior standpoint, the surfactant becomes less water-like when the formulations enter the Winsor Type III region and becomes oil-like when the formulations pass the optimum condition and into the Winsor Type II region. Therefore, in the Winsor Type II region, the surfactant will more favorably adsorb onto the oil and the substrate rather than stay in the bulk solution, and this may hinder the detergency on the wash step even though the IFT is as low as it was in the Type I region. Tongcumpou et al [11-12] observed that if the washed fabrics were rinsed with saline water (same salinity as the wash solution) instead of DI water, detergency efficiencies stayed approximately the same at low salinity region but decreased dramatically at optimum conditions. In the current work, we observed the detergency at the Winsor Type II region after rinses were as low as without rinses if saline water was used (data not shown) instead of DI water. These observations are in agreement with our discussion above. Evaluating this more fully was beyond the scope of the current paper and should be further explored in future research.

Figure 4.3 presents the dynamic IFT values of the after-wash solutions and after-rinse-1 solutions. The IFTs of the after-wash solutions were approximately the same to those of the initial wash solutions, indicating that surfactant adsorption during the wash cycle was minimal for the surfactant concentration of 1000 ppm. The IFTs of the rinse-1 solutions are quite high, varying between 1.3 to 3.9 mN/m. The increase in IFTs in the rinse cycle is likely due to the decrease in surfactant concentration and the change in salinity (de-ionized water was used in the rinse cycle). As suggested by Tongcumpou et al [11-12], the oil removal in the rinse cycle likely followed the snap-off and/or roll-up mechanisms due to the increased IFTs but was still low enough to make the contact angle larger than 90 degree.

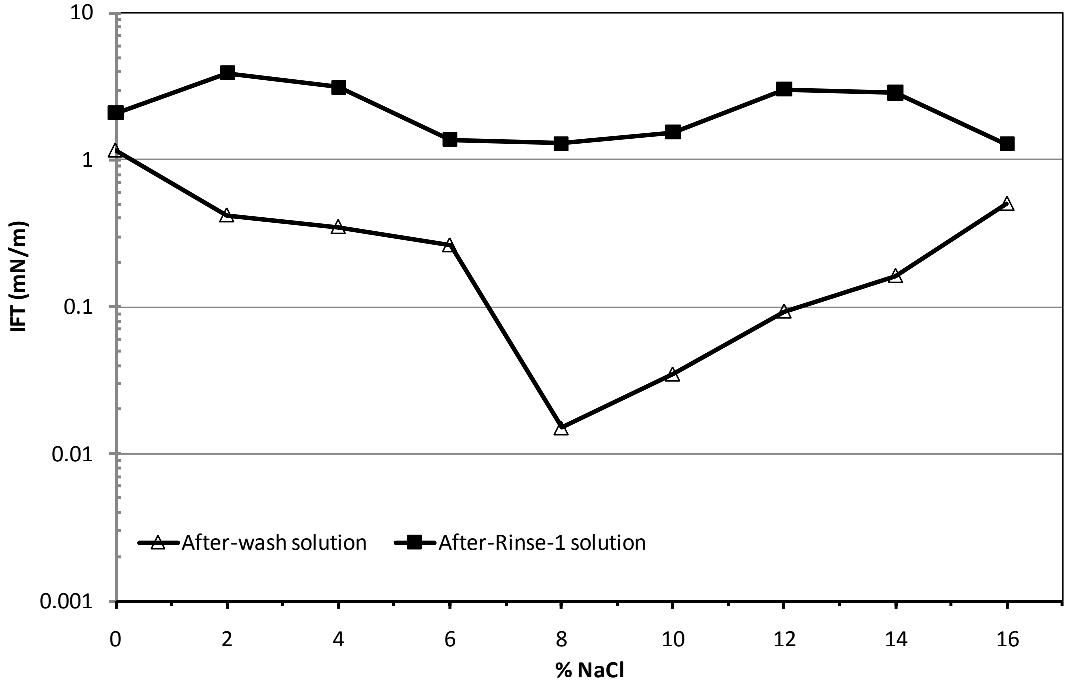


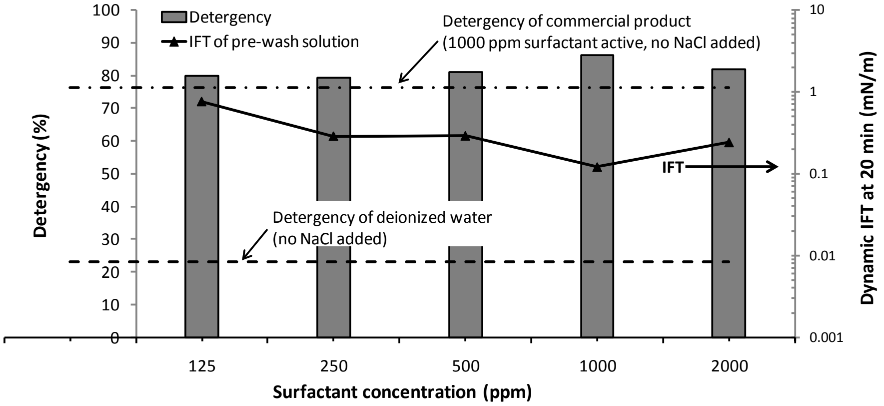
Figure 4.3 Dynamic IFT (at 20 min) of the after-wash solutions and dynamic IFT (at 5 min) of the after-rinse-1 solutions from the full procedure test (20-min wash cycle, 3-min rinse-1 cycle and 2-min rinse-2 cycle). Agitation at 120-rpm, temperature at 25^{o}C, 1,000 ppm $C_{14,15}$-8PO-SO_4Na

As noted above the detergency efficiencies in the Winsor Type II region were higher than those in the Winsor Type III region although the IFTs of the rinse solutions were approximately the same. The reason might be due to the difference in IFTs in the wash cycle. Because the IFTs in the Type III region are significantly lower than those in the Type II region, the spreading effect (oil penetrates into the fabrics) [8, 11-12] may have occurred in the wash cycle in Type III detergency while the spreading effect did not occur in the Winsor Type II region. More work should be done to confirm this speculation. It is also interesting to note that the detergency efficiencies in the Type II region (most of the oil was removed in the rinse cycle) were significantly higher than those in the Type I region (most of the oil was removed in the wash cycle). It is possible that surfactant adsorption at the oil/bath and substrate/bath interfaces in the wash cycle was maximized with the formulations in the Winsor Type II region (the surfactant is oil-like) and desorption of the surfactants with the solubilized oil in the rinse cycle was also maximized because the surfactant was water-like. This chemically-driven work combined with mechanical work from agitation make the oil removal in the rinse cycle would account for more effective detergency. However, further studies should be done to explore this phenomenon.

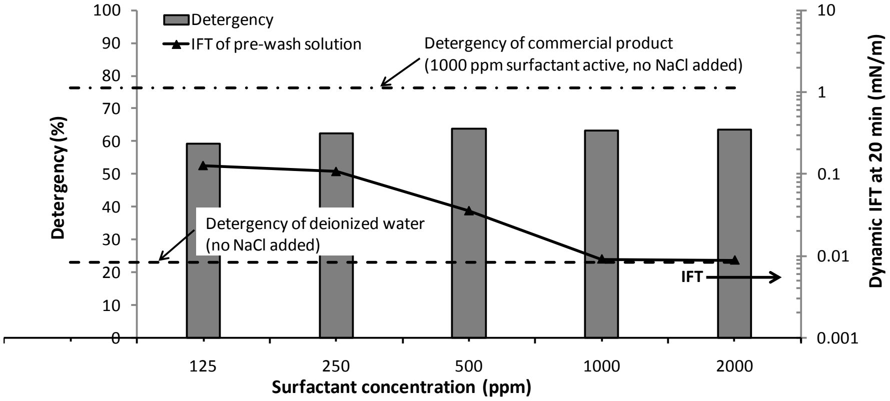
Detergency vs. surfactant concentration

Figure 4.4 presents dynamic IFTs and detergency efficiencies at various surfactant concentrations at 4% NaCl (Type I region), 10% NaCl (Type III) region and 14% NaCl (Type II region). The results show that surfactant concentration has little impact on detergency efficiencies in Type I and Type III regions. It is interesting to observe that at 4% NaCl, the detergency efficiency remained high at surfactant concentration as low as 125 ppm. This observation confirms the suggestion that oil removal in Type I region occurs in the wash cycle through roll-up or snap-off mechanisms due to IFT reduction (IFT=0.12-0.76 mN/m @ 125-2000 ppm). It is also interesting to observe that detergency efficiency in Type III region (10% NaCl) did not improve with increasing surfactant concentrations even though the IFT values increased at the lower surfactant concentrations (IFT=0.13 mN/m at 125 ppm and IFT=0.11 mN/m at 250 ppm). For the Type II region, detergency efficiencies decreased significantly at 125 ppm and 250 ppm (69% and 86% respectively) even though the IFT values are approximately the same. This observation is in line with our speculation that it is the surfactant adsorption in the wash cycle that affects the oil removal in Type II region detergency, i.e. these surfactant concentrations may be too low to achieve the optimum surfactant absorption at the oil surfaces. The above observations again validate the microemulsion-based approach in designing effective detergency formulations while also demonstrating that the best performance is not always coincide with lowest IFTs [8, 12].

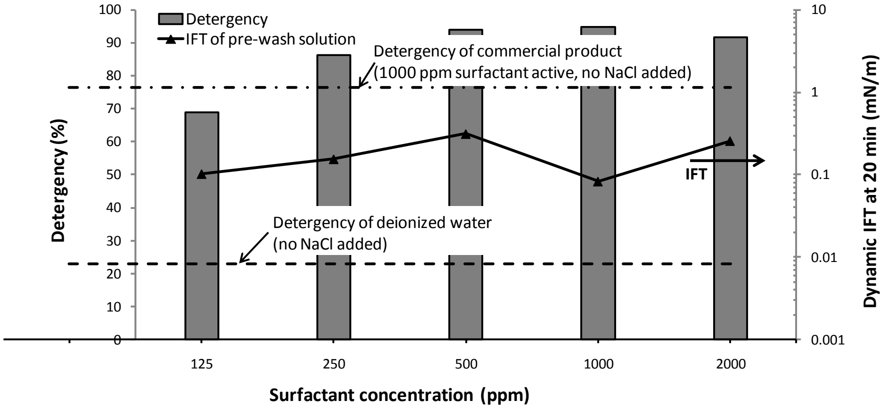
Regardless of which oil removal mechanisms occurred, the surfactant concentrations that provided good detergency with vegetable oils in this work (as low as 125 ppm) are less than the surfactant concentration range (500-2500 ppm) reported in other microemulsion-based detergency work [7-17]. This is attributable to the low CMC and CμC of the extended surfactant (1.4 ppm and 50 ppm respectively, detailed data not shown).



(a) 4% NaCl - Type I



(b) 10% NaCl - Type III



(c) 14% NaCl - Type II

Figure 4.4 Dynamic IFTs (at 20 min) of the wash solutions with canola oil and detergency efficiencies of full procedure test (20-min wash cycle, 3-min rinse-1 cycle and 2-min rinse-2 cycle) at various surfactant ($C_{14,15}$-8PO-SO_4Na) concentrations and salinities (a) 4% NaCl – Type I (b) 10% NaCl – Type III and (c) 14% NaCl – Type II.

In addition, while the salinity range that provided maximum detergency (in Type II region, >14% NaCl) in this work is quite high, one can choose more hydrophobic extended surfactants (longer hydrocarbon chain, more PO group, less hydrophilic head group etc.) to achieve maximum detergency at lower salinities. Thus, microemulsion-based extended surfactant formulations have been shown to be a highly viable approach for vegetable oil detergency toward “green” detergent products with less surfactant and reduced wash temperature. This approach should be further evaluated in future research.

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CHAPTER 5

Conclusions

This dissertation has advanced our understanding of extended surfactant based triglyceride microemulsion and demonstrated the viability of extended surfactant based microemulsion applications through important findings as summarized below.

By systematically studying the effects of triglyceride molecular structure (with different chain length and degree of unsaturation) on optimum conditions (Chapter 2), it is revealed that triglyceride oils with increasing degree of unsaturation (more double bonds) act as more hydrophobic oils (required higher salinity to achieve optimum condition and higher IFT values). Other findings include that the ester group reduces triglyceride oil hydrophobicity as well as that increased chain length of triglyceride impacts optimum conditions (increased optimum salinity but causes little change in IFT values). These findings suggest that the complicated spatial arrangement of triglyceride molecules is an important factor when selecting surfactant systems to solubilize these oils. Another significant contribution from this work is the determination of EACN value of triolein (EACN=19) which appropriately reflects its highly hydrophobic nature.

The study of the impact of extended surfactant (Chapter 3) on microemulsion phase behavior and IFT values with triglyceride oils provided meaningful insights. For the impact of PO group on IFT values, the 8-PO and (14-18)PO-2EO extended surfactants were able to achieve IFT values much less than 0.1 mN/m for canola oil and tricaprylin. However, 4-PO extended surfactants were only able to achieve ultralow IFT with tricaprylin, a short-chain saturated triglyceride tricaprylin C8:0 (EACN=16), but not with canola oil (EACN=18). Optimum salinity values were also lower for the higher PO extended surfactants. In short, extended surfactants with 8-PO or more will be able to achieve ultralow IFT with vegetable oils.

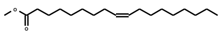
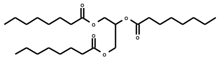
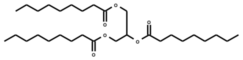
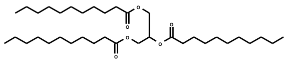
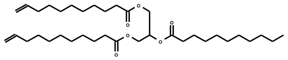
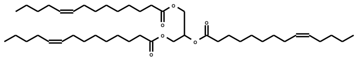
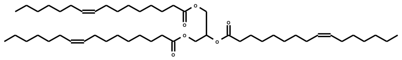
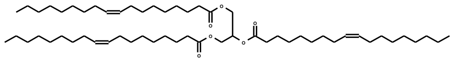
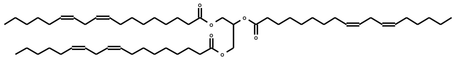
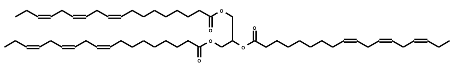
Another interesting and important finding is the effect of degree of branching of hydrocarbon tail of extended surfactants. The results show that the optimum salinity and IFT values are substantially lower with increasing degree of branching in the hydrocarbon tail, speculatively due to the reduced tail-tail interaction between surfactant molecules. Tail branching also appears to play an important role in enhancing triglyceride solubilization through middle phase microemulsion formation as the 8-PO branched extended surfactants were able to form middle phase microemulsion with canola oil but sponge phases were observed instead of middle phase for the (14-18)PO-2EO linear extended surfactants. This observation is interesting because the latter had lower IFT values with both tricaprylin and canola oil. Winsor Type I and Type II microemulsions with tricaprylin and canola oil were also observed for the 8-PO and (14-18)PO-2EO extended surfactants. These observations suggest that polar and bulky molecules like triglyceride molecules need surfactant aggregates large enough and with a desirable environment to accommodate these molecules, i.e. extended surfactants with branched tail and 8-PO or more are required to solubilize triglyceride oils.

Phase behavior studies and IFT measurements (Chapter 4) of a single extended surfactant system $C_{14,15}$-8PO-SO_4Na with canola oil showed that the extended surfactant is a good candidate for microemulsion-based vegetable oil detergency. The surfactant can form Winsor Type I, III and II and can achieve ultralow IFT with canola oil. Detergency tests showed that a single extended surfactant system can achieve detergency > 80% at surfactant concentrations as low as 125 ppm. This work also observed a close relationship between detergency performance, oil removal mechanisms and microemulsion phase behavior and IFT values. Maximum detergency (95%) was observed in the Winsor Type II region with the oil removed mostly in the rinse steps. The secondary most efficient detergency (86%) was observed in Winsor Type I region with oil mostly removed in the wash step. The minimum detergency (63%) was observed at optimum condition (minimum IFT) with most of the oil removed in the rinse step. It is noted that the high detergency efficiencies recorded in this work were achieved at very low surfactant concentration and low temperature (25^oC), an encouraging step toward “green” detergent products.

In summary, with the above findings on the impacts of triglyceride structure and extended surfactant structure on triglyceride oil IFT values and microemulsion formation, one can make use of those findings to optimize extended surfactant systems suitable for many applications, as demonstrated successfully in the case vegetable oil detergency in this work.

Future work on triglyceride microemulsions should exam the role of PO groups in extended surfactant molecules to verify whether the PO groups’ main effect is the extension of the hydrocarbon tail or the intermediate polar nature that causes excellent performance of extended surfactants with triglyceride oils. Further investigation of the effect of hydrocarbon branching in extended surfactant molecules is also needed, i.e. branching at the middle of the hydrocarbon chain or closer to the alcohol carbon would result in better solubilization. Regarding vegetable oil detergency, extended surfactant formulation should be optimized with more hydrophobic extended surfactants (more PO groups…) to lower the salinity needed to achieve good detergency.

APPENDIX A
Nomenclature and Chemical Structure of Methyl Oleate and Common Triglycerides

Oil	Simplified molecular structure	Molecular formulation	MW	Total no. of carbon	Fatty acid chain length	Location of double bonds	No. of double bond in each fatty acid chain
Methyl Oleate		$C_{19}H_{36}O_2$	296.49	19	18	9-cis	1
Tricaprylin		$C_{27}H_{50}O_6$	470.68	27	8	-	0
Trinonanoin		$C_{30}H_{56}O_6$	512.77	30	9	-	0
Triundecanoin		$C_{36}H_{68}O_6$	596.93	36	11	-	0
Triundecenoin		$C_{36}H_{62}O_6$	590.93	36	11	10-cis	1
Trimyristolein		$C_{45}H_{80}O_6$	717.18	45	14	9-cis	1
Tripalmitolein		$C_{51}H_{92}O_6$	801.27	51	16	9-cis	1
Triolein		$C_{57}H_{104}O_6$	885.43	57	18	9-cis	1
Trilinolein		$C_{57}H_{98}O_6$	879.38	57	18	9-cis, 12-cis	2
Trilinolenin		$C_{57}H_{92}O_6$	873.34	57	18	9-cis, 12-cis, 15-cis	3

APPENDIX B

CMC and CμC Data of $C_{14,15}$-8PO-SO_4Na

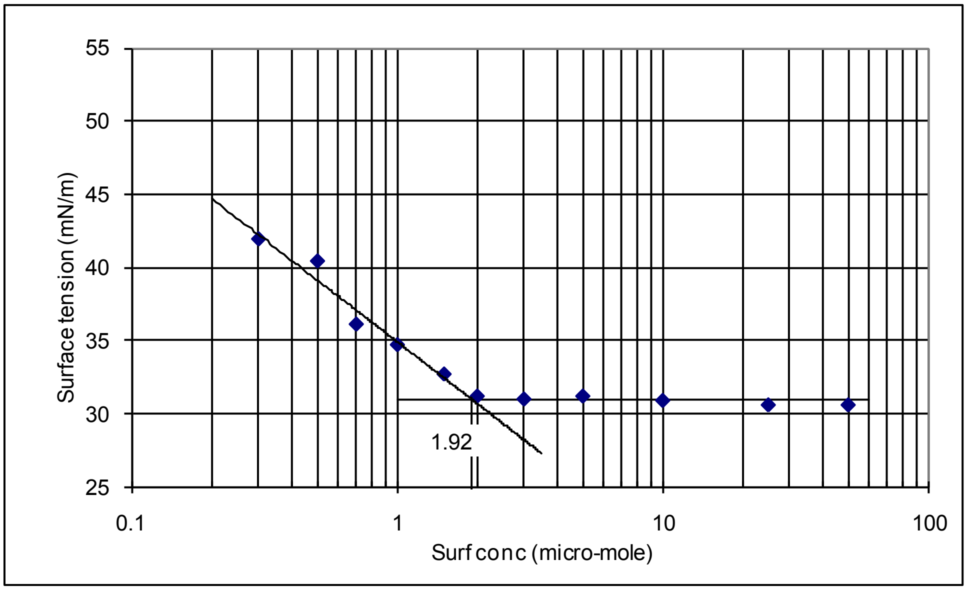


Figure A-1 Surface tension measurements at 25°C to determine CMC of $C_{14,15}$-8PO-SO_4Na. CMC=1.92 μM=1.4 ppm (Chapter 4)

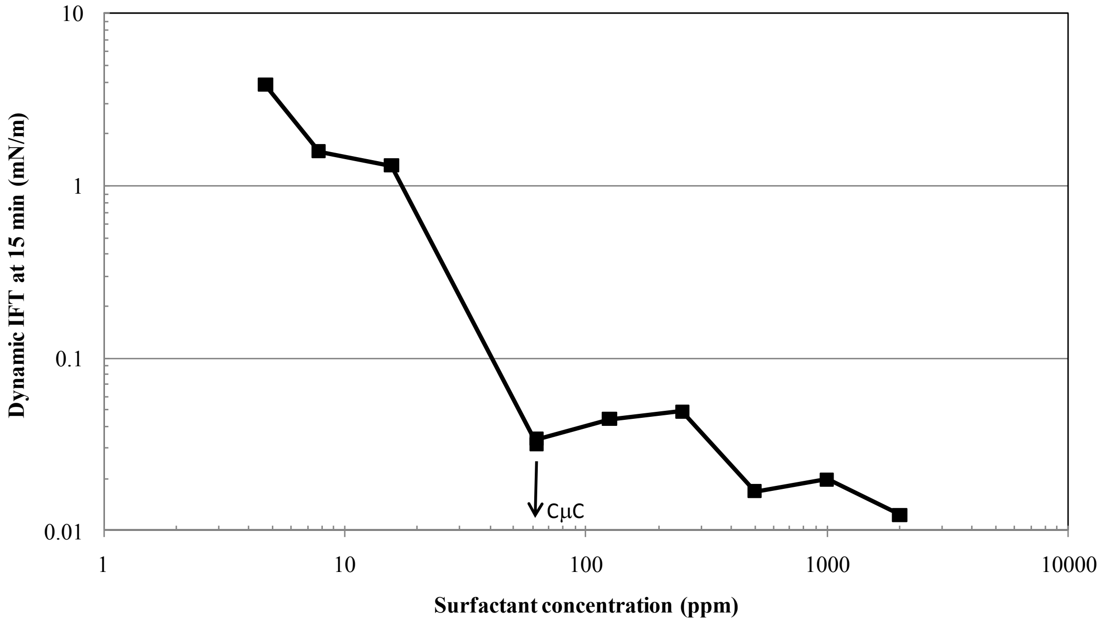


Figure A-2 Interface tension measurements at 25°C to determine CμC of $C_{14,15}$-8PO-SO_4Na. CμC =50 ppm (Chapter 4)

APPENDIX C

Thermodynamic and Kinetic Characteristics of Winsor Type III Microemulsion Formation by Extended Surfactants and Hydrophilic/Lipophilic Linker Systems

Table B-1: Effect of linkers on of thermodynamic and kinetic characteristics of extended surfactant systems; oil: hexadecane; temperature: 25^{o}C; $\xi -$ characteristic length in angstrom

Surfactant system	IFT* (mN/m)	SP* (mL/g)	ξ (A)	Coalescence rate (cm/min)
0.08M $C_{12,13}$-8PO-Sulfate, 50% branching, 50% linear	6.6x10^{-3}	9.4	267	5.0E-03
0.08M $C_{12,13}$-8PO-Sulfate, 50% branching, 50% linear + 0.03M SMDNS	6.0x10^{-3}	4.5	106	1.2E+00
0.08M $C_{12,13}$-8PO-Sulfate, 50% branching, 50% linear + 0.03 M SMDNS + 0.01M Dodecanol	5.0x10^{-3}	7.1	167	6.8E-02
0.08M $C_{12,13}$-8PO-Sulfate, 50% branching, 50% linear + 0.03M SMDNS + 0.01M Oley Alcohol	3.9x10^{-3}	8.6	204	1.9E-02

Table B-2: Effect of branching on thermodynamic and kinetic characteristics of extended surfactant systems; oil: hexadecane; temperature: 25^{o}C; $\xi -$ characteristic length in angstrom

Surfactant system	IFT* (mN/m)	SP* (mL/g)	ξ (A)	Coalescence rate (cm/min)
0.08M $C_{12,13}$-8PO-Sulfate (100% branching) + 0.09M SMDNS + 0.01M Oley Alcohol	0.0037	6.8	157	1.9E-01
0.08M $C_{12,13}$-8PO-Sulfate (50% branching, 50% linear) + 0.09M SMDNS + 0.01M Oley Alcohol	0.0091	2.7	58	6.2E-02

Table A-3: Effect of PO number on thermodynamic and kinetic characteristics of extended surfactant systems; oil: hexadecane; temperature: 25°C; ξ – characteristic length in angstrom

Surfactant system	IFT* (mN/m)	SP* (mL/g)	ξ (A)	Coalescence rate (cm/min)
0.08M $C_{12,13}$-3PO-Sulfate (50% branching, 50% linear)	0.0058	12.3	400	2.4E-02
0.08M $C_{12,13}$-5PO-Sulfate (50% branching, 50% linear)	0.0065	8.5	286	1.6E-02
0.08M $C_{12,13}$-8PO-Sulfate (50% branching, 50% linear)	0.0066	8.2	267	5.0E-03