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DESIGNING AND CHARACTERIZING SURFACTANT FORMULATIONS FOR  
DETERGENCY OF OILY AND SOLID NON-PARTICULATE SOILS

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DESIGNING AND CHARACTERIZING SURFACTANT FORMULATIONS FOR  
DETERGENCY OF OILY AND SOLID NON-PARTICULATE SOILS

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# Table of Contents

Acknowledgement .....	iv
List of Tables .....	x
List of Figures .....	xi
Abstract .....	xiv
Chapter 1 Introduction .....	1
Overview of Chapters.....	6
References .....	8
Chapter 2 Cold water detergency of triacylglycerol semisolid soils: the effect of salinity, alcohol type, and surfactant systems .....	12
Abstract.....	12
Introduction.....	13
Experimental Procedures.....	16
Materials .....	16
Methodology .....	17
Results and Discussion.....	20
Microemulsion phase behavior studies .....	20
Correlation between dynamic IFT measurement and detergency of coconut oil with different salinities .....	20
Correlation between alcohol type, contact angle and dynamic IFT measurements.....	21
The effect of surfactant systems on alcohol selection.....	24
The effect of alcohol type on contact angle of coconut oil in different surfactant systems ..	25
The effect of alcohol types on melting point shift of coconut oil in different surfactant systems .....	26

The effect of triacylglycerol soil molecule.....	27
Optimized surfactant solutions vs. cold water detergency .....	28
Mean particle size and zeta potential measurements of the optimized surfactant solutions ..	31
Conclusions.....	32
Acknowledgements.....	33
References .....	33
Chapter 3 The effect of surfactant systems, alcohol types and salinity on cold-water detergency of triacylglycerol semisolid soil. Part II.....	41
Abstract.....	41
Introduction.....	42
Experimental Procedures.....	45
Materials .....	45
Methodology .....	45
Results and Discussion.....	47
Effect of linear chain and number of EO of surfactant on IFT and S* .....	47
Detergency of coconut oil using various surfactant systems without and with added salt at S* .....	49
Effect of octanol type on S* .....	50
Effect of octanol type on coconut oil removal.....	51
Correlation between detergency and contact angle.....	53
Correlation between detergency and solubilization .....	54
Comparing optimal concentration of 1-octanol and 2-octanol in C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na formulations.....	55
Conclusions.....	57

Acknowledgements .....	57
References .....	58
Chapter 4 Correlation between detergency of different oily and solid non-particulate soils and hydrophilic-lipophilic deviation (HLD) .....	63
Abstract.....	63
Introduction.....	64
Experimental Procedures.....	67
Materials .....	67
Methodology .....	67
Results and Discussion.....	69
Determinations of K and Cc-values for studied surfactant systems .....	69
Determination of EACNs of studied oils for detergency study .....	70
Detergency results: Correlation between detergency of soils, salinity, HLD and IFT using C <sub>10</sub> -4PO-SO <sub>4</sub> Na surfactant as a primary surfactant study .....	72
Correlation between detergency and HLD .....	75
Correlation between detergency of selected soils with EACNs of 5.2 and 16.6, salinity and HLD using a binary surfactant mixture (C <sub>10</sub> -4PO-SO <sub>4</sub> Na and AOT at 1:1 by molar ratio) as a confirmatory surfactant system.....	76
Correlation between detergency of solid octadecane (EACN = 18) and HLD using a binary surfactant mixture between C <sub>10</sub> -4PO-SO <sub>4</sub> Na and AOT at 1:1 by molar ratio .....	78
Conclusions.....	79
Acknowledgements .....	79
References .....	80
Chapter 5 Conclusions .....	84
Appendix A Evaluating the effect of crystal form of solid triacylglycerol on detergency .....	87



Introduction.....	87
Experimental Procedures.....	89
Materials .....	89
Methodology .....	89
Results and Discussion.....	90
Heating rate selection for evaluating tristearin crystal formation.....	90
Crystal formation Results .....	92
Preliminary detergency results on aluminum surface .....	93
Next Steps.....	94
References .....	94
Appendix B Effect of surfactant concentration on detergency of different coconut oil states....	97

## List of Tables

Table 2.1 The properties of studied surfactants and alcohols .....	17
Table 2.2 Contact angle of different surfactant systems .....	26
Table 2.3 Melting point of coconut oil in different surfactant systems (published melting point = 27.5°C) .....	27
Table 2.4 Mean coconut solid particle sizes, zeta potentials and detergency of coconut oil at 10°C in different washing baths .....	32
Table 3.1 Properties of anionic extended surfactants and octanols .....	45
Table 3.2 Oil solubilization study .....	55
Table 4.1 S* for each studied oil using different surfactant systems.....	70
Table 4.2 S* based on IFT measurements, IFT*, and calculated EACNs for all five oils studied	71

## List of Figures

Figure 1.1 Correlation between microemulsion phase behavior and HLD value (modified from Phan et al., 2011). .....	4
Figure 2.1 The correlation between coconut oil dynamic IFT measurement at 30°C and cold water detergency at 10°C as a function of salinity. C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na concentration was kept constant at 0.1 w/v%.....	21
Figure 2.2 Correlation between cold water detergency at 20°C, contact angle measurement at 20°C, and dynamic IFT measurement at 30°C. A series of alcohols at concentration of 90 mM were added in 0.1 w/v% C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na solutions .....	24
Figure 2.3 Coconut oil removal in different surfactant/alcohol systems at a washing temperature of 10°C. All concentrations of surfactants and alcohols remained constants at 0.1 w/v% and 90 mM, respectively.....	25
Figure 2.4 The effect of triacylglycerol soil types on cold water detergency in 0.1 w/v% C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na with the addition of alcohols at a washing temperature of 10°C. These surfactant systems were used without salt.....	28
Figure 2.5 Cold water detergency performance of coconut oil in different 0.1 w/v% C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na/90 mM alcohol (when present) systems at a washing temperature of 10°C.....	30
Figure 2.6 Effect of varying 1-octanol concentration in 0.1 w/v% C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na at 4 w/v% NaCl on cold water detergency of coconut oil .....	30
Figure 3.1 IFT between coconut oil and different anionic extended surfactant systems through dynamic IFT measurement at 30°C. The minimum IFT of each surfactant corresponds to its S* as denoted by ↓. All surfactant concentrations were constant at 0.1 w/v%.....	48
Figure 3.2 Cold water detergency of coconut oil using different anionic extended surfactant systems at 10°C. All surfactant concentrations were constant at 0.1 w/v%. Numbers indicate in the figure are S* for each surfactant formulation.....	50

Figure 3.3 IFT between coconut oil and C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with added different octanol types through dynamic IFT measurement at 30°C. The minimum in IFT of each surfactant corresponds to its S\* as denoted by ↓. Surfactant and octanol concentrations were constant at 0.1 w/v% and 90 mM, respectively.....51

Figure 3.4 Cold water detergency of coconut oil using C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with added various octanol types at 10°C. Surfactant and octanol concentrations were constant at 0.1 w/v% and 90 mM, respectively. Numbers indicate in the figure are S\* for each surfactant formulation. ....53

Figure 3.5 Correlation between detergency and contact angle of various optimized surfactant systems. Surfactant and octanol concentrations were 0.1. w/v% and 90 mM, respectively. ....54

Figure 3.6 The effect of varying additive concentrations on cold-water detergency of coconut oil at 10°C. Surfactant concentration was kept constant at 0.1 w/v%. ....56

Figure 4.1 Plot of ln(S\*) against EACN to determine surfactant characteristics (K and Cc values) for studied surfactant systems.....70

Figure 4.2 Correlation between detergency, salinity, HLD, and IFT for different EACNs of studied soils. **a)** EACN = 5.2, **b)** f EACN = 7.5, **c)** EACN =10.1, **d)** EACN =12.8, and **e)** EACN = 16.6. Detergency studies (bar charts) and dynamic IFT measurements (line charts) were all conducted using 0.1 w/v% C<sub>10</sub>-4PO-SO<sub>4</sub>Na at 25 ± 1°C. The horizontal dash lines indicate IFT with 1 mNm<sup>-1</sup>. ....75

Figure 4.3 Correlation between detergency and HLD for all studied soils using 0.1 w/v% C<sub>10</sub>-4PO-SO<sub>4</sub>Na. Washing temperature was kept constant at 25 ± 1°C. The horizontal lines indicate a location of 80% removal. The vertical dash lines indicate an HLD region between -3.0 and 0.0. ....76

Figure 4.4 Detergency of soils with EACNs of **a)** 5.2 and **b)** 16.6 at various salinity levels and corresponding HLD values using a binary surfactant mixture of C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio. Washing temperature was kept constant at 25 ± 1°C. The horizontal lines indicate a location of 80% removal. The vertical dash lines indicate an HLD region between -3.0 and 0.0. ....77

Figure 4.5 Correlation between detergency of octadecane (solid non-particulate soil), salinity and HLD using the binary surfactant mixture of C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio. Detergency experiment was done at 25 ± 1°C. Reported melting point temperature of octadecane is 26 - 29°C. The horizontal lines indicate 80% removal. The vertical dash lines indicate an HLD region between -3.0 and 0.0. .... 79

Figure A-1 Effect of heating rate on DSC thermogram of tristearin. About 1 mg tristearin was heated to 100°C, held at 67°C for 2 hours, and cooled to 25°C using cooling rate of 0.2°C/min. The samples were then heated to 80°C using heating rates of **a)** 30°C/min **b)** 50°C/min **c)** 70°C/min, respectively. Upward peak indicates endotherm and downward peak indicates exotherm. .... 91

Figure A-2 Effect of aging time on alpha to beta tristearin transition using heating rate of 70°C/min ..... 92

Figure A-3 Effect of aging time on beta tristearin formation using heating rate of 70°C/min ..... 93

Figure A-4 DSC thermogram of post-wash alpha sample. Detergency was carried out for 20 minutes at 20°C. Heating rate was 70°C/min. .... 94

Figure B-1 IFT measurements using C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with 8 w/v% NaCl at 30°C. .... 97

Figure B-2 Surface tension measurements at 30°C. Surfactant system studied was C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with 8 w/v% NaCl. .... 98

Figure B-3 Correlation between detergency of liquid and semisolid coconut oil and IFT at different surfactant concentrations. Surfactant concentrations of C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na was varied with the addition of salt at 8 w/v% NaCl. .... 99

## Abstract

Laundry detergency is a complex process at the nexus of soil, surfactant, solid substrate, and wash condition. This dissertation contains the following two major topics. The first topic focused on developing surfactant formulations capable of providing effective cold-water detergency of coconut oil below its melting point. While the cold-water detergency of coconut oil below its melting point on 65/35 polyester/cotton surface was poor using a 0.1 w/v% branched C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na surfactant alone, coconut oil removal was found to be higher with the addition of intermediate chain alcohols (C7-C9 alcohols) than those of shorter and longer alcohols. Further detergency improvement was observed with added salt at optimum salinity (S\*). Octanol was selected as an intermediate chain alcohol representative to evaluate detergency with the presence of branched octanols (2-octanol and 2-ethyl-hexanol) in the surfactant formulation. The interfacial tensions (IFT) measurement between the surfactant and melted coconut oil revealed that the S\* required decreased from 8 w/v% NaCl for no alcohols to 4 w/v% NaCl for 1-octanol and to 2 w/v% NaCl for 2-octanol and 2-ethyl-hexanol. Comparing cold-water detergency using the surfactant system with added S\*, the detergency of coconut oil increased from roughly 49% removal for no alcohol with 8 w/v% NaCl, to 83% removal for 2-ethyl-hexanol with 2 w/v% NaCl, to 95% removal for 1-octanol with 4 w/v% NaCl, and to 98% removal for 2-octanol with 2 w/v% NaCl. Further, optimized surfactant formulations were tested with the effect of alcohol concentration as a final optimization study. Decreasing 1-octanol concentration from 90 mM (1.2%) to 15.3 mM (0.2%) and 2-octanol from 90mM (1.2%) to 38.5 mM (0.5%), their detergency still retained exceeding 90% removal. This work found that improved detergency of coconut oil below its melting point appeared to associate with a reduction in IFT (below 1 mNm<sup>-1</sup>), enhanced wetting of the soil surface, and increasing solubilization of the removed soil in surfactant micelles. However, the studies of melting point alteration and dispersion stability were not found to correlate to enhanced detergency.

The second topic of this research attempted to demonstrate a correlation between detergency of a wide range of soils and surfactant-systems hydrophilic-lipophilic deviation (HLD) values. Two anionic surfactant systems (C<sub>10</sub>-4PO-SO<sub>4</sub>Na and a binary mixture of C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio) were characterized surfactant characteristics using HLD concept. The results

suggested that the single C<sub>10</sub>-4PO-SO<sub>4</sub>Na surfactant was more hydrophilic than the mixed surfactant system due to more negative C<sub>c</sub> value. Detergency using a 0.1 w/v% C<sub>10</sub>-4PO-SO<sub>4</sub>Na surfactant was first conducted using five different oily soils with widely varying equivalent alkane carbon numbers (EACNs) from 5.2 to 16.6 (ranging from low to high hydrophobicity). The detergency was conducted at different NaCl concentrations corresponding to HLD values, ranging from negative (Type I microemulsion), to zero (optimum Type III microemulsion), and to positive (Type II microemulsion). The detergency increased with increasing NaCl concentrations (beginning at HLD = -3 for most cases), reached a maximum at its S\* (HLD = 0), and decreased with further increasing NaCl concentrations over the S\* (HLDs > 0). Effective oily soil removal (> 80% removal) was observed at widely varying NaCl concentrations which corresponded to an identical HLD range between -3 and 0 with IFTs below 1 mNm<sup>-1</sup>. The mixture of C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT was then studied as a confirmatory surfactant system. Likewise, the detergency trend was observed with varying NaCl concentrations and the HLD range between -3 and 0 showed excellent detergency of studied soils (lowest and highest EACNs). Finally, the mixed surfactant system was further evaluated detergency of octadecane (EACN = 18, solid non-particulate at 25°C) and demonstrated that detergency using surfactant systems with the HLD values between -3 and 0 was superior than other HLD ranges. Thus, this work suggests the utilization of HLD concept as a valuable tool for designing optimum detergency formulations for a wide range of soils.

## Chapter 1 Introduction

The global laundry detergency market is anticipated to reach over 100 billion dollars by 2026 (Market Study Report, 2016). Laundry detergency formulations have been extensively studied to develop and improve their cleaning performance to meet the customer needs. The research problem surrounding laundry detergency is attempting to meet the challenge of attaining a detergency formulation capable of providing effective detergency performance under specified conditions. Previous work has shown that detergency performance varies depending upon the nature of surfactant, soil, solid substrate, water hardness, and washing temperature (Arai, 1966; Attaphong and Sabatini, 2017; Chi and Obendorf, 2001). In recent years, the trend of detergency research has moved toward the use of sustainable ingredients and low washing temperatures to reduce adverse environmental impact.

Soil removal mechanisms have been associated with multiple processes regarding the type of soil. Most studies agree that soil can be classified into 3 major types; oily, solid particulate and solid non-particulate soils (sometimes referred to as semisolid soil). Previous work has illustrated that removal mechanisms of each soil type were found to be different. Oily soils (e.g. vegetable-based oils and motor oil), that are liquid at a wash temperature, are mainly removed by roll-up and snap-off mechanisms (Miller and Raney, 1993; Tongcumpou et al., 2005). The adsorption of surfactant reduces the interfacial tensions (IFTs) between soil/surfactant and fabric/surfactant, causing the soil to roll-up and detach itself from fabric. Solid particulate soils (e.g. activated carbon, silica, and sand) are dominantly removed by the IFT reduction of solid/bath and an increased electrical potential induced by surfactant adsorption (Harris, 1961; Rojvoranun et al., 2012). Lastly, solid non-particulate soils (e.g. butter and lard) exhibit a unique property. These soils have a mixture of solid and liquid portions (Timms, 1985) in which the liquid matrix is entrapped in the solid matrix below their melting point (Chanwattanakit et al., 2017). This unique property of the solid non-particulate soil hinders its removal by surfactant adsorption. In particular, the removal mechanisms of solid non-particulate soils are not well understood and have been shown to be more complicated than those of other soils.

In the removal process, the adsorption and penetration of surfactant has been shown to be primary steps to modify microcrystal structure of the soil (also known as the softening or liquefaction step)



resulting in wetting alteration of the soil (Cox, 1986). A softened soil could then be dislodged from the fabric surface with agitation applied. Under these circumstances, the soil removed was found to be small amounts of solubilized fractions in micellar aggregates of the bulk aqueous solution (Chanwattanakit et al., 2017a; Kabin et al., 1996; Kawase et al., 1991). The majority of removed particles were stably dispersed in the wash solution by electrostatic repulsion of the surfactant preventing redeposition on the fabric (Chanwattanakit et al., 2017).

Surfactant (Surface Active Agent) is one of essential ingredients in detergents to remove stains (soil) from fabric surface. Because of their negative charges, anionic surfactants have been extensively used in laundry detergent to help prevent the removed soil from redepositing on the cleaned fabric by electrostatic repulsive force of the surfactant head group. Another superior anionic surfactant property is temperature insensitivity (Velásquez et al., 2010) which is crucial in the laundry detergent. However, other studies found that cleaning performance of anionic surfactants is salt-dependent (Attaphong and Sabatini, 2017). Recently, anionic extended surfactants with insertion of intermediate polar groups (polyethylene oxide, (EO) and polypropylene oxide (PO)) have been introduced to overcome the disadvantages of conventional surfactants. Such surfactants provide higher solubilization as a consequence of lowering interfacial tension (IFT) between oil and surfactant (Miñana-Perez et al., 1995). This was found to be desirable for detergency performance (Do et al., 2015; Tanthakit et al., 2010).

Alcohols can be utilized in cleaning applications to further enhance soil removal by several mechanisms. The role of alcohol was dependent upon a function of alkyl chain length and can be categorized into 3 types (Graciaa et al., 1993). Short-chain alcohols (<C6 alcohols) favorably adsorb near palisade layer and counter-ion, thus diluting surfactant concentration at interface and lowering solubilization. Intermediate-chain alcohols (C6-C10 alcohols) preferentially partition to the oil-water interface near the surfactant tail providing additional interaction to the oil phase, further enhancing solubilization (lowering IFT), and reducing  $S^*$  required. Longer-chain alcohols (>C10 alcohols) are no longer adsorbed at the interface and behave as an oil co-solvent (Sabatini et al., 2003). When 90mM oleyl alcohol and 180 mM dimethyl naphthalene sulfonate (SMDNS) were added to a 4 w/v% sodium bis (2-ethyl) dihexyl sulfosuccinate (AOT) with 5 w/v% NaCl, it was found that motor oil removal was enhanced from roughly 30% to over 85% with the addition of the additives. (Acosta et al., 2003)

Microemulsions are thermodynamically stable systems of aqueous and oil phases and can be classified into three types (Rosen and Kunjappu, 2004) as depicted in Fig. 1.1. A Winsor Type I microemulsion has oil solubilized in normal micelle of aqueous phase with low salinity for anionic surfactant and low temperature for nonionic surfactant. With increasing salinity or temperature, maximum solubilization of water and oil is attained in the middle phase which is known as a Winsor Type III microemulsion or middle phase microemulsion. For a Winsor Type II microemulsion, surfactant solubilizes in the oil phase and forms reverse micelles with further increasing salinity or temperature. Improved detergency formulations have been demonstrated to correlate with microemulsion phase behavior (Phan et al., 2010; Tongcumpou et al., 2003; Tongcumpou et al., 2006). Tongcumpou et al. (2003) showed that optimal salinity range varied depending upon studied soils. Effective hexadecane and motor oil removal was found at 5-8% NaCl and 12-16% NaCl, respectively, corresponding to the  $S^*$  region (Type I approaching optimum Type III microemulsions) with IFTs below 1 mN/m. In a comparison of  $S^*$  ranges of the same oil using two different surfactant systems, the maximum canola oil removal was observed at 14% NaCl using  $C_{14-15}-8PO-SO_4Na$  (Phan et al., 2010) and 2.5 w/v% NaCl using a binary surfactant mixture of  $C_{10-18}PO-2EO-SO_4Na$  and dioctyl sodium sulfosuccinate (AOT) at 0.26:0.74 molar ratio (Do et al., 2015). Thus, an optimum surfactant formulation was observed to be influenced by the hydrophilic/hydrophobic nature of the surfactant system and oil.

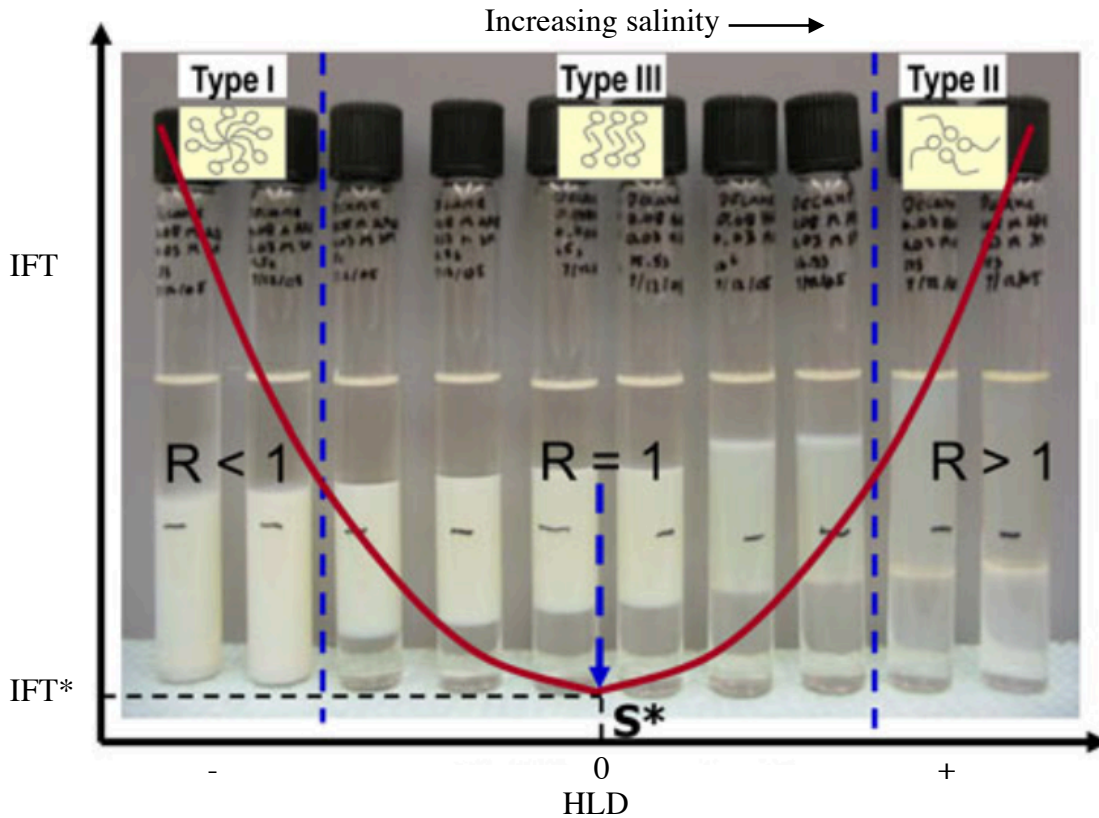


Figure 1.1 Correlation between microemulsion phase behavior and HLD value (modified from Phan et al., 2011).

Salager et al. (1979) proposed a hydrophilic lipophilic deviation (HLD) concept to quantitatively describe microemulsion phase behavior. The HLD values explain deviation from the optimum Winsor Type III of surfactant formulation ( $S^*$ ). Negative, zero, and positive values of HLD correspond to Winsor Type I, optimum III, and II microemulsions, respectively. The HLD equations can be classified into 2 types depending on surfactant head group:

Anionic surfactant

$$\text{HLD} = \ln(S) - K \times \text{EACN} - f(A) - \alpha\Delta T + Cc \quad (1.1)$$

Nonionic surfactant

$$\text{HLD} = bS - K \times \text{EACN} - f(A) - c\Delta T + Cc \quad (1.2)$$

Where  $S$  is salinity of the aqueous phase (g NaCl/100 mL),  $b$  is salt dependence for nonionic surfactant which found to be approximately 0.13 for NaCl (Acosta, 2008).  $K$  is a function of

surfactant head group which is reported to a range of 0.1 - 0.2 (Acosta et al., 2008; Hammond and Acosta, 2012; Salager et al., 1979; Velásquez et al., 2010; Witthayapanyanon et al., 2008). (E)ACN is the (equivalent) alkane carbon number describing the hydrophobic/hydrophilic nature of the oil; for example, hexane has an ACN (EACN) of 6 and canola oil has an EACN of 17 (Do et al., 2009). The hydrophobicity of oil increases with increasing EACN.  $f(A)$  is a function of alcohol or cosolvent, if present, and depends on the alcohol type and concentration.  $\alpha$  is a temperature coefficient (typically is  $0.01 \text{ K}^{-1}$  for most anionic surfactants (Broze, 1999; Hammond and Acosta, 2012; Salager et al., 1979).  $c$  is a temperature constant for nonionic surfactants (generally is  $0.06 \text{ K}^{-1}$ ) (Acosta, 2008).  $\Delta T$  is the difference between the studied temperature and reference temperature ( $T-25^\circ\text{C}$ ). The  $C_c$  value describes the relative hydrophilic/lipophilic nature of the surfactant. A negative  $C_c$  value corresponds to a hydrophilic surfactant which preferably forms normal micelles in the aqueous phase. In contrast, a positive  $C_c$  corresponds to a hydrophobic surfactant which favors the formation of reverse micelle in oil phase (Acosta et al., 2012; Witthayapanyanon et al., 2008).

The goals of this dissertation are to design and characterize detergency formulations for a wide range of soils and to provide a proof of removal mechanism concept. Following are the main objectives of this dissertation:

1. Investigate surfactant formulations (effects of salinity and alcohol type) capable of providing effective cold-water detergency of triacylglycerol solid non-particulate soils below their melting point temperatures, as well as, to evaluate fundamental removal mechanisms (Chapter 2)
2. Further explore surfactant formulations (surfactant structure, salinity, and branched alcohol) for cold-water detergency of triacylglycerol solid non-particulate soil below its melting point and explore removal mechanisms (Chapter 3)
3. Examine the utility of HLD as a unifying design approach for detergency of oily and solid non-particulate soils with varying hydrophobic/lipophilic natures (Chapter 4)

## Overview of Chapters

Chapter 2 discusses the first objective of this research: to study the effect of salinity and alcohol type as a surfactant additive to improve cold-water detergency of triacylglycerol solid non-particulate soils. Cold-water detergency was performed at washing temperatures (10°C and 20°C) below solid non-particulate soil's melting point. Coconut oil was employed as a primary soil and palm kernel oil was used as a confirmatory soil. The detergency experiments were carried out on a 65/35 polyester/cotton surface. A branched anionic extended surfactant ( $C_{14-15}$ -8PO-SO<sub>4</sub>Na) was used as a primary surfactant system. Due to poor detergency of coconut oil using the surfactant with added salt at  $S^*$ , a series of alcohols (2-butanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol) were further introduced in the surfactant system to study the detergency improvement. Further, a single  $C_{10-16}$ -7EO-OH and a binary surfactant mixture of  $C_{10-18}$ PO-2EO-SO<sub>4</sub>Na+SDOSS at 0.24/0.76 by molar with 0.5 w/v% NaCl (Do et al., 2015) were investigated as confirmatory surfactant systems. The studies of IFT, contact angle (wetting), melting point alteration, particle size, and zeta potential (dispersion stability) were conducted to determine correlation with detergency performance.

Chapter 3 attempts to further investigate the effect of varying  $C_{14-15}$ -8PO-SO<sub>4</sub>Na based surfactant structure and branched alcohol on cold-water detergency of coconut oil (second objective). A series of 50% linearity (L) with varying intermediate hydrophilic ethylene oxide (EO) groups ( $LC_{14-15}$ -8PO-SO<sub>4</sub>Na,  $LC_{14-15}$ -8PO-3EO-SO<sub>4</sub>Na, and  $LC_{14-15}$ -8PO-7EO-SO<sub>4</sub>Na) were conducted to compare detergency performance with the branched  $C_{14-15}$ -8PO-SO<sub>4</sub>Na (previously studied in Chapter 2). Comparing detergency of coconut oil using different  $C_{14-15}$ -8PO-SO<sub>4</sub>Na based-surfactant structures, the branched  $C_{14-15}$ -8PO-SO<sub>4</sub>Na still showed better coconut oil removal. Thus, the branched  $C_{14-15}$ -8PO-SO<sub>4</sub>Na surfactant was further used to study the effect of branched alcohols. Since the introduction of intermediate-chain alcohols (C7-C9 alcohols) in the surfactant systems showed superior coconut oil removal than those of other alcohol types, octanol was selected as a representative of intermediate-chain alcohol to examine the effect of branched alcohols (2-octanol and 2-ethyl-hexanol). The studies of IFT, contact angle (wetting), and oil solubilization were investigated to see how they correlated with improved detergency.

Chapter 4 is a second topic in this dissertation as a pioneer study in the correlation between detergency of oily and solid non-particulate soils and HLD concept (third objective). Two surfactant systems ( $C_{10}$ -4PO-SO<sub>4</sub>Na and a binary mixture of  $C_{10}$ -4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio) were utilized to conduct detergency of different oils with varying hydrophilic/lipophilic natures which is also referred to as equivalent alkane carbon numbers (EACNs). Before performing detergency experiments, the surfactant systems were characterized for HLD parameters (K and C<sub>c</sub> values) through microemulsion phase behavior studies. Five different oils were then studied with hydrophobicities or EACN values varying from 5.2 to 16.6 (ranging from low to high hydrophobicities). Detergency studies were conducted on a 65/35 polyester/cotton surface at a washing temperature of 25°C. Detergency of all oily soils using the  $C_{10}$ -4PO-SO<sub>4</sub>Na was first studied with varied salt concentrations from lower than S\*, at S\* and higher than S\*. All salt concentrations were then converted to HLD values varying from negative, to zero, and to positive values using eq. 1.1. The measurements of IFT between surfactant and oil phases were performed to examine IFT for each surfactant formulation. Detergency of soils with lowest and highest EACN values was then carried out at different HLD values using the binary mixture of  $C_{10}$ -4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio. The detergency results of oily soils using two different surfactant systems were found at widely different salinities but corresponded to an identical HLD range from -3 to 0. Finally, detergency of solid non-particulate soil (octadecane) using the mixed surfactant system was performed to verify if the HLD range of -3 to 0 can be adopted for detergency of a studied solid non-particulate.

Chapter 5 summarizes the main findings of this research and suggests potential ideas for future research.

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## Chapter 2 Cold water detergency of triacylglycerol semisolid soils: the effect of salinity, alcohol type, and surfactant systems

### Abstract

Cold water detergency of triacylglycerol semisolid soils is much more challenging than liquid vegetable oils due to poorer interaction between surfactant and semisolid soil. This research seeks to improve the removal efficiency of semisolid soils below their melting points using surfactant-based formulations containing different alcohol additives. To this end, cold water detergency of solid coconut oil and solid palm kernel oil was investigated in various surfactant/alcohol systems, including single anionic extended surfactant, single nonionic alcohol ethoxylate surfactant and a mixture of anionic surfactants. A series of alcohols (2-butanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol) was added to the surfactant formulations to investigate cold water detergency improvement. While cold water detergency using surfactant alone was poor, it was considerably improved when optimum salinity ( $S^*$ ) and 1-heptanol, 1-octanol or 1-nonanol were introduced to the studied surfactant formulations. The maximum detergency of solid coconut oil exceeded 90% removal in 0.1w/v% C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na/0.2w/v% 1-octanol/4w/v% NaCl system (a final optimized surfactant system) at washing temperature of 10°C versus 22.9±2.2% in surfactant alone (not at optimum salinity and no additive). Further analysis showed that improved cold water detergency using surfactant/intermediate-chain alcohols/NaCl could be correlated with high wettability (low contact angle) as well as favorable surfactant system-soil interaction as observed by lower interfacial tension values. In contrast, the improved cold water detergency was observed to be independent of dispersion stability. This work thus demonstrates that surfactant system design, including additives, can improve cold water detergency of semisolid soils and should be further explored in future research.

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## Introduction

Vegetable oils are mainly composed of triacylglycerol with different carbon chain lengths. A triacylglycerol is a triester of glycerol with three fatty acid molecules. The long and bulky fatty acid alkyl chains account for the nonpolar portion (hydrophobic moiety) of the triacylglycerol, while the ester groups of glycerol account for the polar portion (hydrophilic moiety). Below their melting point, triacylglycerols are semisolid soils. Detergency of these soils is challenging because removal of semisolid soil is impeded by the liquid oil being entrapped in the crystalline solid fat (Timms, 1985; Do et al., 2015) resulting in poor removal efficiency (Cox, 1986; Illman et al., 1970).

Laundry activities consume not only water but also energy to heat water. Schmitz & Stamminger (2014) investigated the annual energy consumption per washing cycle in European countries and found that the average electrical energy consumption was reduced 2.5 times by decreasing the washing temperature from 50 to 20°C. This energy saving motivates the pursuit of improved surfactant systems for cold water detergency.

Anionic surfactants have been widely used in household laundry products to remove grease and oils while mitigating redeposition of the removed soil (Cox et al., 1985; Favrat et al., 2013). More recently, anionic extended surfactants have been introduced to overcome the limitations of conventional anionic surfactants in cleaning systems. The major disadvantages of conventional anionic surfactants are their high critical micelle concentration (CMC), precipitation at high salt and hardness levels and poor solubilization of large organic molecules (Stellner & Scamehorn, 1986; Miñana-Perez et al., 1995; Do et al., 2009). In contrast, anionic extended surfactants have stronger surfactant-oil interaction with the presence of polypropylene oxide (PO) groups and stronger surfactant-water interaction with the insertion of polyethylene oxide (EO) groups. For this class of surfactants, PO and EO groups are inserted between the head and tail groups of conventional surfactants, thus extending the molecules further into either oil phase or aqueous phase, thus the name extended surfactants. The intermediate insertion of PO and EO groups also promotes a smoother transition between the hydrophilic and hydrophobic regions of the surfactants resulting in increased salt and hardness tolerance. Furthermore, this superior surfactant structure has been shown to provide greater solubilization in microemulsions while also achieving ultralow

interfacial tension (IFT) ( $<10^{-3}$  mN/m) with vegetable oils (Aoudia et al., 2006; Do & Sabatini, 2010; Phan et al., 2010).

For detergency of liquid vegetable oils, Do et al. (2009) compared the use of conventional anionic surfactant (sodium dioctyl sulfosuccinate, SDOSS) and anionic extended surfactant ( $C_{12-14}PO-2EO-SO_4Na$ ) on the dynamic IFT of triolein. The dynamic IFT results showed that SDOSS was not able to reach ultralow IFT, while  $C_{12-14}PO-2EO-SO_4Na$  could produce ultralow IFT with triolein. In addition, nonionic surfactants are also widely used in cleaning systems due to their salt and hardness tolerance (Lee et al., 2016) as well as high efficiency in non-polar organic soil removal (Dillan et al., 1979; Dillan, 1984). However, their removal performance is temperature-dependent which is undesirable in practice (Thompson et al., 1996; Huibers & Shah, 1997). Previous research has found that the maximum vegetable oil removal was observed with the lowest IFT providing the maximum oil solubilization capacity. For ionic surfactants, the maximum soil removal was found near/at optimum salinity ( $S^*$ ) (Tongcumpou et al., 2003; Tanthakit et al., 2010), while for nonionic surfactants, it was attained near phase-inversion temperature (PIT) (Raney & Miller, 1987; Thompson, 1994).

Oily soil removal is typically attributed to the roll-up and snap-off mechanisms (Miller & Raney, 1993; Kabin et al., 1998; Tongcumpou et al., 2005). In general, surfactant molecules adsorb on the fabric surface as well as solubilize/emulsify the oil. These steps take place during the washing cycle. During the rinse steps, roll-up or liquid crystal formation occurs to facilitate the detachment of oil droplets from the solid substrate by a reduction in IFT between the soil and the bath as a consequence of an increase in the contact angle of the attached oil droplet (Tongcumpou et al., 2005). Ideally, complete oily soil detachment from the solid substrate appears when the contact angle approaches  $180^\circ$  (complete roll-up).

In contrast, semisolid soil detergency is an extremely complicated process simultaneously involving many physiochemical processes. Scheuing (1990) reported that the removal of tri-stearin soil was more complicated than those of solid alkane soils because the polymorphism in the solid crystal of tri-stearin hindered the soil removal by surfactant molecules. The dominant removal mechanism of myristic acid by sodium dioctyl sulfate (SDS) and alcohol ethoxylate surfactant with 7 groups of EO was accomplished by micellar solubilization of the myristic acid below its

melting point (Kawase et al., 1991; Kawase et al., 1994). In later studies, semisolid soil removal was achieved by surfactant penetration promoting loosening of the soils and subsequent solubilization (Beaudoin et al., 1995; Kabin et al., 1996; Kabin et al., 1999). Recently, Chanwattanakit et al. (2017) found that methyl palmitate was not removed through roll-up mechanism but rather detached by the surfactant-enhanced-wetting. This mechanism is the process of weakening of the particle's failure strength cause by solubilization-emulsification leading to the soil being dislodged into small fractions, followed by dispersion into the bath (Bourne & Jennings, 1963; Grindstaff et al., 1967).

Generally, the detergency of semisolid soils is fairly poor at low washing temperatures. For example, a recent study in cold water detergency of methyl palmitate shows that it achieved about 25% removal at 15°C and 30% removal at 20°C in 0.1wt% C<sub>12-13</sub>-4PO-SO<sub>4</sub>Na at 5wt% NaCl (an optimized surfactant formulation) (Chanwattanakit et al., 2017). In an effort to improve detergency performance, incorporation of alcohol additives to the surfactant system is being considered in this research. Alcohols have been used as surfactant additives in liquid laundry detergency, enhanced oil recovery (EOR) and pharmaceutical applications (McKarns et al., 1997; Acosta et al., 2003; Salager et al., 2017).

Short-chain alcohol molecules have been mixed in surfactant-oil mixtures in order to produce a low viscosity microemulsion and prevent separated viscous phase formation (Graciaa et al., 1993; Graciaa et al., 1993; Hirasaki et al., 2011). Further, short-chain alcohols such as propanol favorably solubilize in palisade layer near the surfactant heads and counterions, thus reducing surfactant film rigidity and accelerating approach to equilibrium (Hirasaki et al., 2011). Intermediate-chain alcohols preferentially solubilize in both the palisade layer and the micelle core providing an additional interaction to the oil phase which results in enhanced oil solubilization capacity (Acosta et al., 2003). Longer-chain alcohols can act as lipophilic linkers and enhance the microemulsion behavior (decreased IFT and increased solubilization) (Sabatini et al., 2003). It has been found that oil removal efficiency was enhanced by the addition of long-chain alcohol in the surfactant formulation; e.g., motor oil removal was approximately 30% in 4w/v% SDOSS with 5w/v% NaCl, while it went up to over 85% with an addition of 90 mM oleyl alcohol and 180 mM sodium mono and dimethyl naphthalene sulfonate (SMDNS) to the surfactant formulation (Acosta et al., 2003).

Thus, this current study focuses on developing optimized surfactant formulations that provide improved cold water detergency of triacylglycerol semisolid soils. The main objectives of this work are to investigate the effect of optimum salinity ( $S^*$ ), alcohol type (intermediate- to long-chain alcohols) and surfactant systems on improving cold water detergency while also evaluating fundamental system properties for correlation with detergency (IFT, contact angle, melting point shift, particle size and zeta potential).

## **Experimental Procedures**

### ***Materials***

While most studies were conducted using coconut oil from *Cocos nucifera*, a confirmatory study was also conducted with palm kernel oil. The coconut oil and alcohols studied (2-butanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol) were all purchased from Sigma Aldrich (St. Louis, MO, USA). Palm kernel oil was purchased from Mountain Rose Herbs (Eugene, OR). The reported melting points of coconut and palm kernel oils are 27.5°C (current study) and 28.6°C (Do et.al., 2015), respectively. The anionic extended surfactant used in this study was a branched alcohol propoxylate sulfate sodium salt with 14-15 carbon atoms with 8 groups of propylene oxide (PO) ( $C_{14-15}-8PO-SO_4Na$ ) with 93.84% active, as received from Sasol North America, Inc. (Lake Charles, LA, USA). The branched surfactant dioctyl sodium sulfosuccinate (SDOSS, 80%) was purchased from Sigma Aldrich (St. Louis, MO, USA). The linear anionic extended surfactant with 18 PO and 2 EO groups ( $C_{10}-18PO-2EO-SO_4Na$ ) with 21.5% active was received from Huntsman Chemical Co. (Houston, TX, USA). Alcohol ethoxylate nonionic surfactants were used as follows: 10-16 carbon numbers with 7 and 9 groups of ethylene oxide (EO) ( $C_{10-16}-7EO-OH$  and  $C_{10-16}-9EO-OH$ ) and 100% active, as supplied by Huntsman Chemical Co. (Houston, TX, USA). The physical properties of the selected surfactants and alcohols are shown in Table 2.1. The oil-soluble dye Oil-Red-O was purchased from Sigma Aldrich (St. Louis, MO, USA). Sodium Chloride (NaCl) with 99% purity was received from Avantor Performance Materials, Inc. (Center Valley, PA, USA). Blended 65/35 polyester/cotton with 34 inch in size was supplied by Test Fabrics, Inc. (West Pittston, PA, USA). All materials and chemicals were performed without further purification. All the solutions were prepared using de-ionized (DI) water.

Table 2.1 The properties of studied surfactants and alcohols

Chemicals	% Purity	Density (g cm <sup>-3</sup> )	Molecular weight (g mole <sup>-1</sup> )	Melting point (T <sub>m</sub> , °C)
<u>Surfactants</u>				
C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na	93.84	1.04-1.07	787	-
C <sub>10-16</sub> -7EO-OH	100.0	0.99	508	-
C <sub>10-16</sub> -9EO-OH	100.0	0.99	596	-
C <sub>10-18</sub> PO-2EO-SO <sub>4</sub> Na	21.5	1.04	1392	-
Diocetyl sodium sulfosuccinate (SDOSS)	80.0	-	444.56	-
<u>Alcohols</u>				
2-butanol	99.5	0.808	74.12	-115
1-hexanol	98.0	0.814	102.14	-52
1-heptanol	98.0	0.822	116.2	-36
1-octanol	98.0	0.827	130.23	-15
1-nonanol	98.0	0.828	144.27	-5
1-decanol	99.0	0.829	158.28	5-7

## ***Methodology***

### *Microemulsion Phase Behavior Studies*

Microemulsion phase behavior studies of liquid coconut oil were carried out by varying the surfactant formulations and NaCl concentrations to observe middle phase microemulsion formation. Five mL of 2w/v% surfactant in aqueous phase was prepared at different salinities, then 5 mL of melted coconut oil (at 30°C) was added in a 15 mL flat-bottom vial to obtain an aqueous surfactant solution-to-oil volumetric ratio of unity. All vials containing the mixtures were gently shaken by hand for once a day for 3 days and placed in a temperature controlled water bath for months to ensure equilibrium at 30°C (above coconut oil's melting point).

### *Dynamic Interfacial Tension (IFT) Measurements*



Dynamic IFT experiments were conducted to evaluate the IFT between the surfactant formulations and melted coconut oil at 30°C (above the melting point) using a spinning drop tensiometer purchased from the University of Texas (Model 500). A volume of 1-3µL melted coconut oil (at 30°C) was injected into a 300-µL capillary tube filled up with a surfactant solution having different NaCl concentrations and alcohol types. Surfactant and alcohol concentrations were kept constant at 0.1w/v% and 90 mM, respectively. The drop radius was recorded every 5 minutes for 20 minutes after oil injection corresponding to the washing period in detergency experiments. The IFT was calculated using the following equation given by Vonnegut (1942),

$$\gamma = \frac{(\rho_1 - \rho_2)\omega^2 R^3}{4}$$

Where  $\rho_1 - \rho_2$  is the difference in densities between the heavy and light phases,  $\omega$  is angular velocity (radius/second) and R is the radius of the cylindrical drop, as measured in the instrument.

#### *Contact Angle Measurements*

Contact angle measurements of surfactant solution against soil surface (solid coconut oil) were carried out by the sessile drop technique at ambient temperature of 20±2°C. An aliquot of approximately 2 µL of the surfactant solution containing the same solutions as those of the washing solutions was dropped on the solid coconut oil coated on the fabric using a micro-syringe and the contact angle was measured after 30 seconds (Chanwattanakit et al., 2017).

#### *Melting Point Determination Studies*

Melting point of coconut oil in surfactant formulation was determined by visual observation. Solid dyed-coconut oil was heated at 30°C, then 0.5 mL liquid dyed-coconut oil was added into a flat-bottom vial. The liquid dyed-coconut oil was allowed to solidify before use overnight at ambient temperature. Five mL of the surfactant formulation was then added into the vial. The oil:water ratio was 1:10 by volume. All the vials were kept in a temperature controlled water bath varying temperature over time. Melting point was recorded as the temperature where the coconut oil completely melted.

#### *Particle Size and Zeta Potential Measurements*

Suspended particle size and dispersion stability measurements of the surfactant formulations after

washing cycle for 20 minutes at 10°C were carried out at day 1 and day 8 to evaluate the time-dependent nature of this property. Particle size and zeta potential were studied with dynamic light scattering (DLS) using a Zeta Plus Analyzer (Brookhaven Instruments Corp. Holtsville, NY) equipped with a 532 nm laser. These experiments were repeated in triplicate for 2 minutes each cycle at measuring temperature of 10°C.

### *Detergency Experiments*

#### 1. Soiling Procedure

Detergency studies were conducted using 3×4-inch swatches of blended 65/35 polyester/cotton in zig zagged direction. Liquid coconut oil was mixed at 20vol% chloroform. Coconut oil was heated at 30°C (above its melting point) prior to mix with chloroform. The swatches were completely submerged in the oil/chloroform solution for one minute and hung to dry overnight in a fume hood before use. All swatches were freshly prepared with the average weight ratios of oil: fabric approximately 0.30±0.02:1 for solid coconut oil and 0.29±0.02:1 for solid palm kernel oil.

#### 2. Detergency Procedure

Cold water detergency was carried out at temperatures of 10°C and 20°C. Detergency experiments were carried out using a Terg-O-Tometer (Model 7243; USA Testing Co., Inc., Hoboken, NJ). A 20-minute wash cycle was performed for washing cycle with 1 L surfactant solution. A 3-minute first rinse and a 2-minute second rinse were performed with 1 L DI-water. Washing and rinsing cycles were at 120 rpm agitation speed. The bath temperature was kept constant during the washing and rinsing steps. Finally, washed fabrics were hung overnight to dry. The detergency was determined by dividing the mass of removed soil after wash to the mass of initial oil soiled. All laundry experiments were repeated in triplicate and the error bars presented in the detergency results were standard deviations that calculated using Microsoft Excel 2016.

## Results and Discussion

### *Microemulsion phase behavior studies*

Based on previous studies, the branched anionic extended surfactant  $C_{14-15}-8PO-SO_4Na$  was initially used in this work since it has been shown to achieve ultralow IFT and high solubilization capacity with liquid triacylglycerol oils (Do et al., 2009; Phan, et al., 2010; Witthayapanyanon et al., 2010) and demonstrated improved cold water detergency performance of canola oil (Attaphong & Sabatini, 2017). Coconut oil was used as a semisolid soil which has melting point of 27.5°C. Figure 2.1 demonstrates that microemulsion phase transition from Type I to III to II was achieved by scanning NaCl from 0 to 13w/v% NaCl at 30°C with 2w/v%  $C_{14-15}-8PO-SO_4Na$ . The phase behavior results show that Type I microemulsion was produced from 0-1w/v% NaCl, Type III microemulsion was observed from 4 to 10w/v% NaCl and Type II microemulsion was observed beyond 9w/v% NaCl with the optimum surfactant system observed at 8w/v% NaCl (optimum salinity ( $S^*$ )).

### *Correlation between dynamic IFT measurement and detergency of coconut oil with different salinities*

Dynamic IFT experiments were carried out to assess interfacial dynamics of the optimum salinity ( $S^*$ ) at 30°C (above coconut oil's melting point). The IFT values were measured after oil injection every 5 minutes for 20 minutes, the latter time corresponding to the studied washing cycle. The IFT measurement as a function of time indicated that the IFT reached the equilibrium after 10 minutes for all salinity values (results not shown). This result suggests that a washing cycle for 20 minutes is long enough to allow surfactant adsorption on the soil-water interface in the bath. The detergency results of the  $C_{14-15}-8PO-SO_4Na/8w/v\%$  NaCl system at 10°C showed that solid coconut oil removal increased with increasing salinity reaching a maximum of 49.4±0.2% at 8w/v% NaCl (the  $S^*$ ), then it decreased at salt concentration beyond the  $S^*$  (Fig. 2.1). Other researchers have observed a similar trend in increased detergency when the microemulsion phase approached Winsor Type III region (Tongcumpou et al., 2003; Phan et al., 2010). The maximum solid coconut oil removal in the surfactant system at 10°C also corresponded to the formation of optimum middle phase microemulsion (Winsor Type III) with the minimum IFT of 0.064 mN/m

at 30°C, as shown in Fig. 2.1. Witthayapanyanon et al. (2006) found that the minimum IFT value of triolein in 10 mM C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na was IFT > 10<sup>-3</sup> mN/m for all salt concentrations. These current results suggest a good correlation between microemulsion phase behavior, IFT studied at temperatures above coconut oil's melting point and cold water detergency efficiency below coconut oil's melting point. In contrast, Chanwattanakit et al. (2017) observed that the best cold water detergency of methyl palmitate did not correspond to optimum salinity above its melting point; reasons for this disparity are not clear.

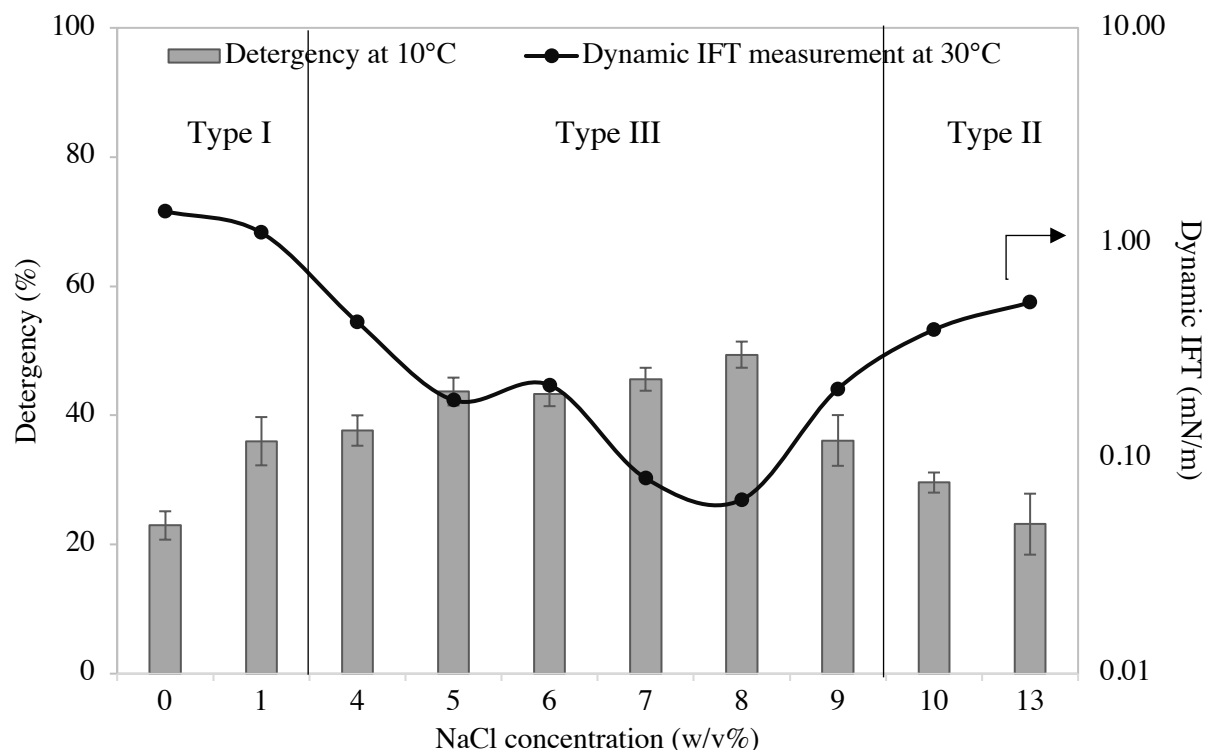


Figure 2.1 The correlation between coconut oil dynamic IFT measurement at 30°C and cold water detergency at 10°C as a function of salinity. C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na concentration was kept constant at 0.1 w/v%.

### ***Correlation between alcohol type, contact angle and dynamic IFT measurements***

In this work, intermediate- to long-chain alcohols (2-butanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol and 1-decanol) were introduced as additives in C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na formulations to evaluate the ability of alcohol addition to improve cold water detergency of solid coconut oil. To

determine optimum alcohol concentration for cold water detergency, 1-octanol was first introduced at varying concentrations as an alcohol representative (in C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na without adding NaCl). The detergency results showed that solid coconut oil removal plateaued for 1-octanol concentrations above 90 mM (results not shown); thus all the alcohol concentrations were maintained constant at 90 mM. Figure 2.2 demonstrates that addition of intermediate-chain alcohol (1-heptanol (C7), or 1-octanol (C8)) in C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na significantly improved solid coconut oil removal to as high as 85% versus ~20% with no alcohol (surfactant only) at 20°C. Meanwhile, shorter- (C6) or longer-chain (C9) alcohols showed poorer detergency of solid coconut oil relative to C7 and C8 alcohols.

Surfactant system adsorption and corresponding change in wettability (Wasan et al., 1988) are considered to be a potential mechanism of surfactant penetration into the soil to loosen the soil molecules (Gotoh et al., 2016; Kanasaki et al., 2016). Higher penetration of the surfactant and corresponding water into the soil phase has demonstrated improved detergency based on the improved ability to wet and penetrate into the soil (Cox et al., 1987). Wettability was assessed by contact angle measurement of a surfactant drop against the solid soil surface. Previous research has demonstrated that a correlation between contact angle and detergency of solid soils (Kalak & Cierpiszewski, 2015; Kanasaki et al., 2016). Smaller contact angle (<90°) corresponds to higher wettability (Wasan et al., 1988). In this current study, a decline in contact angle was observed over measuring time with the different rates depending on the surfactant system so this study was designed to be observed at the same timeframe for all surfactant systems. Results in Fig. 2.2 show that as contact angle decreased (as wetting increased), the detergency improved; however, above the minimum contact angle, the detergency performance declined. Interestingly, for the surfactant formulations with 1-nonanol or 1-decanol, their contact angle values were comparable to formulations with 1-heptanol or 1-octanol but their detergency efficiencies were slightly different.

Solubilization-emulsification is another potential mechanism by which surfactant can improve soil removal. As mentioned above, alcohols modify the surfactant-oil interaction at the interface, thus possibly allowing displacement of the soil molecules and improved soil removal efficiency (Lim et al., 1992). Higher solubilization capacity of oil by surfactant micelles has been shown to correlate with lower IFT values (Wasan et al., 1988; Graciaa et al., 1993; Graciaa et al., 1993; Salager et al., 1998). Dynamic IFT measurements were carried out to determine correlation

between solubilization of surfactant-alcohol-oil mixtures and cold water detergency of solid coconut oil. Figure 2.2 illustrates that cold water detergency at 20°C was maximum with the addition of 1-heptanol or 1-octanol although the IFT value of 1-heptanol at 30°C was about four times higher than that of 1-octanol (1.37 mN/m vs 0.35 mN/m). Previous work observed that 1-hexanol to 1-decanol less preferentially adsorbed at the interface but they provided additional interaction to the oil as a consequence of an increase in oil solubilization capacity (Graciaa et al., 1993). In addition, Kahlweit et al. (1990) investigated the thermodynamic basis for the effect of alcohols on microemulsion formation which found that intermediate- to long-chain alcohols reduced the effective carbon number of oil leading to an observation of the minimum IFT (maximum oil solubilization) at lower temperatures. It could be further observed that the addition of alcohols in C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na was not able to produce an ultralow (<10<sup>-3</sup> mN/m) IFT range with liquid coconut oil. These results are consistent with past research that has shown good detergency as long as IFT values were reduced to the 0.1 to 1.0 mN/m range (Tongcumpou et al., 2003; Tanthakit et al., 2010; Attaphong & Sabatini, 2017) (i.e., ultralow IFT values are not required for good detergency which is attributed to the mechanical agitation/energy present in a washing cycle which promotes roll-up and snap-off mechanisms (Tongcumpou et al., 2005; Phan et al., 2010). These results suggested that wettability and low IFT by surfactant/alcohol mixtures are possible mechanisms to explain the improved cold water detergency. Furthermore, the effect of bath temperatures (at 10°C and 20°C) on cold water detergency with the presence of alcohols was also investigated. It was shown that the detergency showed the same trend at both washing temperatures but the efficiencies were higher at 20°C (Fig. 2.2). This can be attributed to the fact that the fraction of the soil that is liquid is higher at higher temperatures (Do et al., 2015; Chanwattanakit et al., 2017).

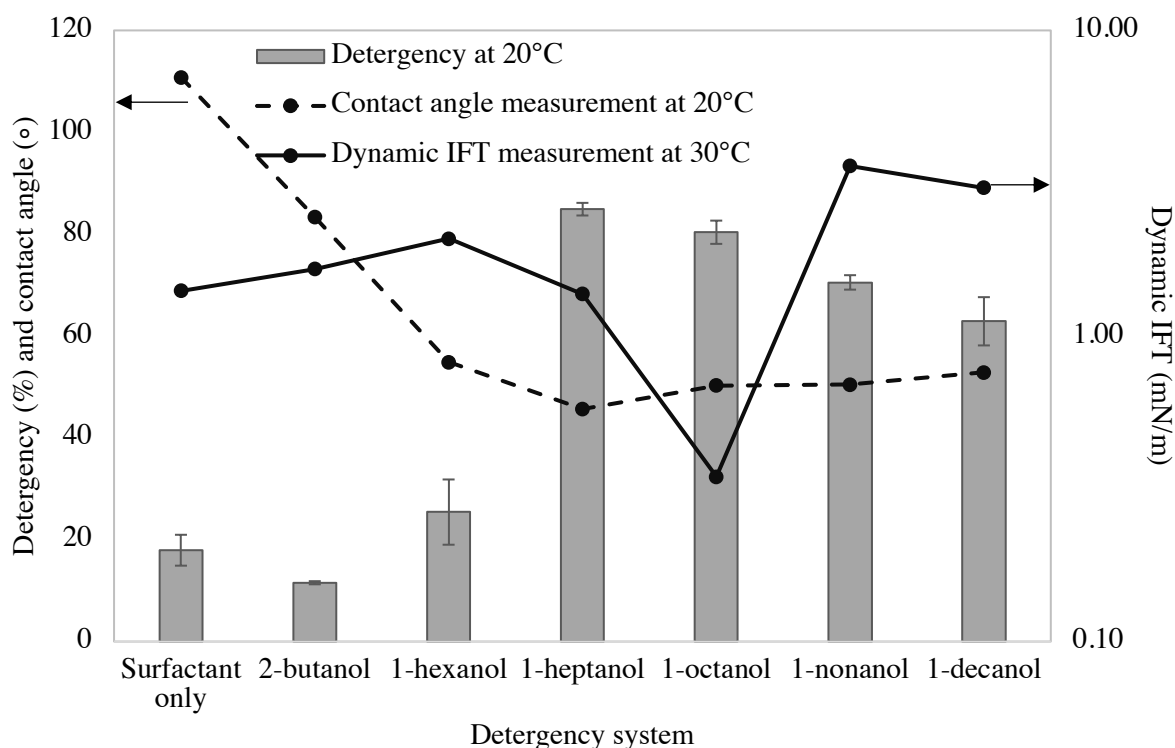


Figure 2.2 Correlation between cold water detergency at 20°C, contact angle measurement at 20°C, and dynamic IFT measurement at 30°C. A series of alcohols at concentration of 90 mM were added in 0.1 w/v% C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na solutions

### ***The effect of surfactant systems on alcohol selection***

The effect of varying the surfactant system on the impact of alcohol addition was also taken into consideration. The surfactant systems of C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na, C<sub>10-16</sub>-7EO-OH (better solid coconut oil removal than C<sub>10-16</sub>-9EO-OH according to this current study, data not shown) and C<sub>10</sub>-18PO-2EO-SO<sub>4</sub>Na+SDOSS at 0.24/0.76 molar fraction with 0.5w/v% NaCl (an optimized surfactant formulation in previous study (Do et al., 2015) were selected to evaluate the impact of alcohol addition on solid coconut oil detergency. Figure 2.3 shows that adding intermediate-chain alcohols (1-heptanol or 1-octanol or 1-nonanol) achieved the most significant level of solid coconut oil removal improvement for all three surfactant systems, demonstrating the robust nature of these alcohols as detergency additives. Exact reasons for the significant change in detergency performance from 1-hexanol to 1-heptanol in C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na are not clear at this time and will

be the subject of future research.

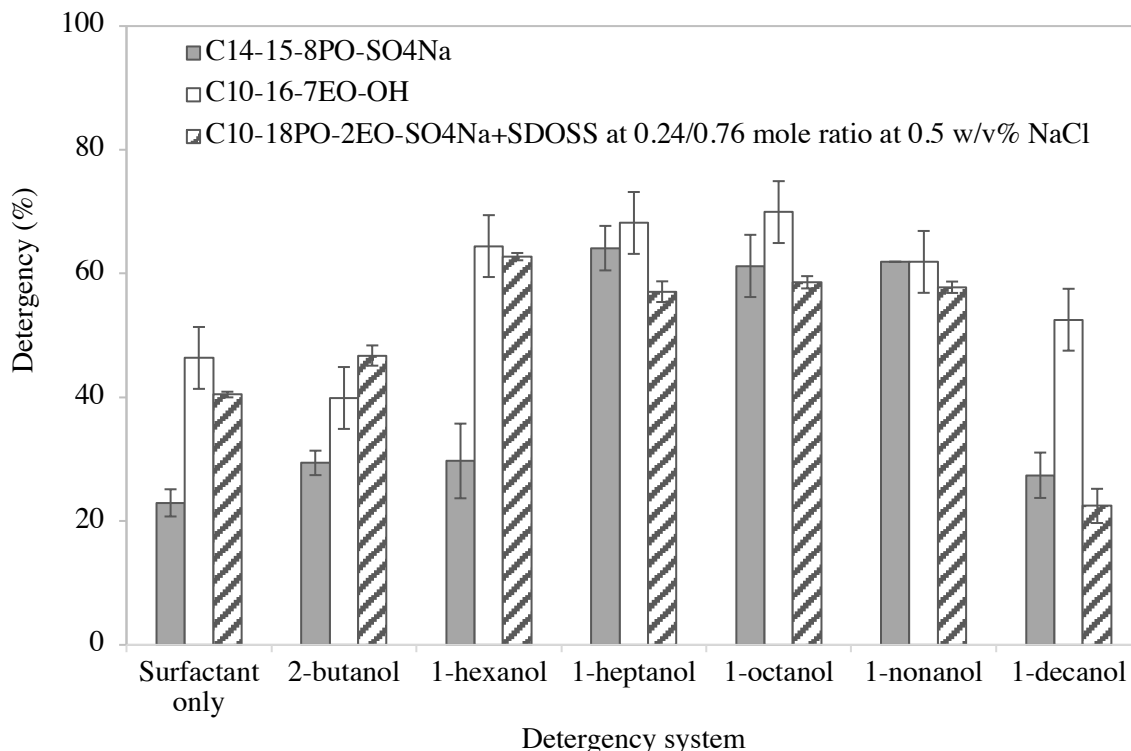


Figure 2.3 Coconut oil removal in different surfactant/alcohol systems at a washing temperature of 10°C. All concentrations of surfactants and alcohols remained constants at 0.1 w/v% and 90 mM, respectively.

***The effect of alcohol type on contact angle of coconut oil in different surfactant systems***

Table 2.2 summarizes contact angle results of the different surfactant formulations. It was found that good cold water detergency of C<sub>14-15-8PO-SO<sub>4</sub>Na</sub> (see Fig. 2.3) for 1-heptanol to 1-nonanol corresponded to the minimum contact angle values of approximately 45.7-50.5°. Meanwhile, the contact angle values for these alcohols in C<sub>10-16-7EO-OH</sub> and C<sub>10-18PO-2EO-SO<sub>4</sub>Na+SDOSS</sub> at 0.24/0.76 molar fraction with 0.5w/v% NaCl were in the ranges of 32.5-43.5° and 52.6-55.8°, respectively. It should be noted that for all three surfactant systems, solid coconut oil detergency was maximum for alcohol systems correlated with lower contact angles (better wetting). Karvan et al. (2011) investigated the correlation between contact angle and detergency performance in nonionic and cationic surfactants and found that contact angles of the hydrophobic surface were



varied from 36.9° to 45.6°. However, contact angle values in this current study were slightly different. This variation somewhat depends on the properties of surfactant, fabric and soil studied (Kalak & Cierpiszewski, 2015). It was also observed that the addition of 2-butanol, or 1-decanol demonstrated higher contact angle values corresponding to poorer cold water detergency. This is consistent with Kalak & Cierpiszewski (2015) which found that the good detergency of activated carbon (a particulate soil) in various surfactant systems was highly related to low contact angle. Contact angle is thus identified as an important parameter for design of optimized detergency formulations in cold water detergency of semisolid soils.

Table 2.2 Contact angle of different surfactant systems

Detergency system	Contact angle (°)		
	C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na	C <sub>10-16</sub> -7EO-OH	C <sub>10-18</sub> PO-2EO-SO <sub>4</sub> Na+SDOSS at 0.24/0.76 molar fraction with 0.5w/v% NaCl
Surfactant only	110.8±0.6	48.3±1.3	61.6±0.7
2-butanol	83.4±0.5	55.0±1.6	56.0±0.9
1-hexanol	54.8±0.7	36.2±1.3	51.7±0.2
1-heptanol	45.7±0.2	35.4±0.9	55.8±0.5
1-octanol	50.3±0.7	32.5±0.4	52.6±0.5
1-nonanol	50.5±0.5	43.5±3.6	55.6±0.7
1-decanol	52.9±0.3	50.1±0.4	58.2±1.5

***The effect of alcohol types on melting point shift of coconut oil in different surfactant systems***

Another potential explanation for the alcohol impact on detergency of semisolids is that they may lower the coconut oil's melting point rendering the soils more oil like. Table 2.3 shows the melting point values measured for different surfactant/alcohol systems (note that the variability in melting point is 2°C or less for all systems). The surfactant formulations without alcohol had similar values of coconut oil melting point temperature. Interestingly, the presence of 1-heptanol or 1-octanol or 1-nonanol did not significantly alter the melting point of coconut oil even though they showed a

marked improvement in cold water detergency. Thus alcohol-lowered melting point is not shown to be a mechanism responsible for the enhanced cold water detergency of our systems.

Table 2.3 Melting point of coconut oil in different surfactant systems (published melting point = 27.5°C)

Detergency system	Melting point (°C)		
	C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na	C <sub>10-16</sub> -7EO-OH	C <sub>10-18</sub> PO-2EO-SO <sub>4</sub> Na+SDOSS at 0.24/0.76 molar fraction with 0.5w/v% NaCl
Surfactant only	27.4±0.1	27.0±1.0	27.6±0.8
2-butanol	26.8±0.0	26.2±0.5	25.3±0.2
1-hexanol	27.0±0.2	26.4±0.3	26.5±0.3
1-heptanol	27.3±0.5	26.6±0.2	26.7±0.3
1-octanol	27.4±0.3	27.0±0.3	26.7±0.3
1-nonanol	28.8±0.2	27.4±0.5	26.9±0.4
1-decanol	28.9±0.5	27.7±0.3	27.0±0.5

### *The effect of triacylglycerol soil molecule*

To confirm our work above with solid coconut oil, limited studies were conducted with solid palm kernel oil to assess the enhanced cold water detergency with intermediate-chain alcohol additives with a second soil. Coconut oil ( $T_m=27.5^\circ\text{C}$ ) and palm kernel oil ( $T_m=28.6^\circ\text{C}$ ) are predominantly composed of lauric acid (C<sub>12:0</sub>) in the range of 45-55% and different portions of other minor components (Young, 1983; Orsavova et al., 2015). Figure 2.4 shows the detergency of solid coconut and solid palm kernel oils in C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with different alcohol types showed a similar trend of removal but slightly different in absolute soil removal efficiencies due to different fatty acid compositions. This study confirmed that the intermediate-chain alcohols were promising additives in cold water detergency of more than one triacylglycerol semisolid soil. Future work will extend these results to a wider range of solid triacylglycerol oils.

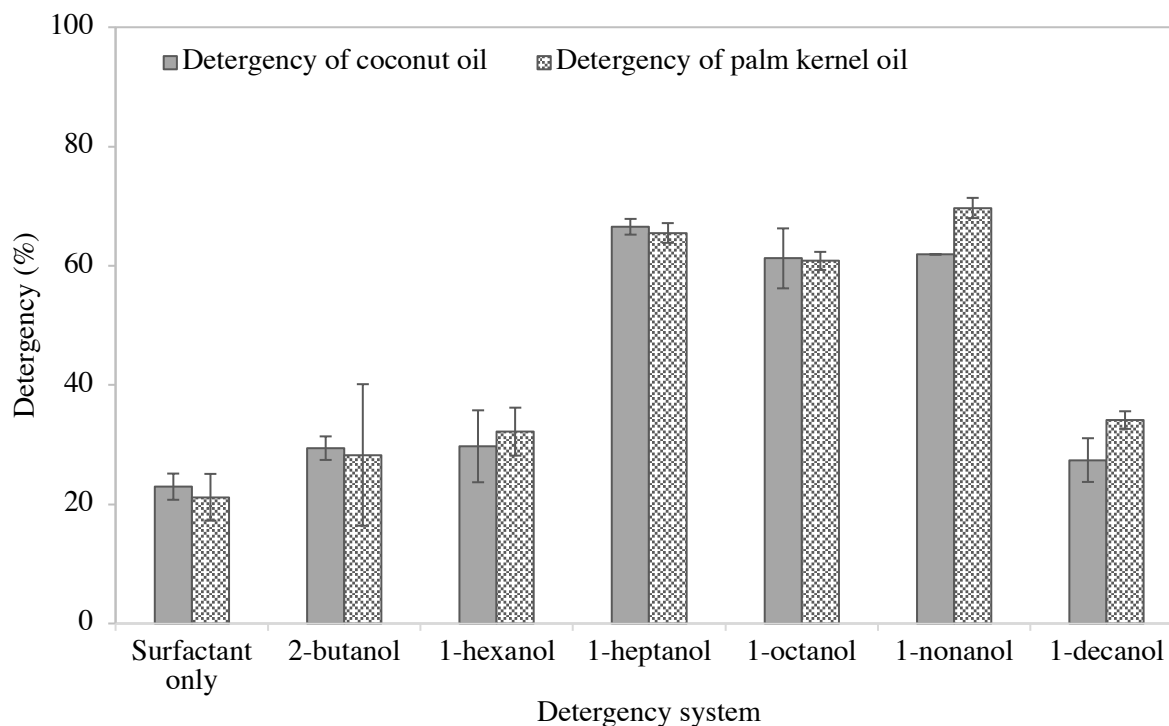


Figure 2.4 The effect of triacylglycerol soil types on cold water detergency in 0.1 w/v% C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with the addition of alcohols at a washing temperature of 10°C. These surfactant systems were used without salt.

### ***Optimized surfactant solutions vs. cold water detergency***

The overall goal of this study was to determine the optimized surfactant formulations providing good cold water detergency of triacylglycerol semisolid soils. It has previously been shown that alcohols modified the nature of surfactant-oil microemulsions such as hydrophobicity/hydrophilicity, oil solubilization capacity, rigidity of surfactant-oil interface and equilibrium rate (Lim et al., 1992; Graciaa et al., 1993; Tien & Bettahar, 2000; Mondal et al., 2017). Nguyen & Sabatini (2009) studied microemulsion of diesel using a mixture of SDOSS and rhamnolipid (JBR) biosurfactant at 23°C. The study showed that the optimum salinity ( $S^*$ ) was reduced from 9.5wt% to 4.25wt% NaCl when 50 mM oleyl alcohol was added to the surfactant system. Their results agreed with previous works (Acosta et al., 2003; Sabatini et al., 2003) that long-chain alcohols increased hydrophobicity of surfactant-oil mixture meaning that  $S^*$  was

reduced.

According to previous studies, research was conducted to identify the adjusted  $S^*$  ( $S^*_{new}$ ) corresponding to the optimized surfactant formulation when alcohol was introduced in the surfactant formulation. The surfactant systems with added 2-butanol (lowest improved detergency performance) and added 1-octanol (most improved detergency performance) were selected to investigate the effect of optimizing the surfactant formulations on cold water detergency. Dynamic IFT measurements were conducted to determine  $S^*_{new}$ , since a good correlation between IFT and cold water detergency was observed in earlier study. Figure 2.5 shows cold water detergency of solid coconut oil in different detergency formulations; DI-water (no surfactant),  $C_{14-15}$ -8PO-SO<sub>4</sub>Na with no added alcohol,  $C_{14-15}$ -8PO-SO<sub>4</sub>Na/8w/v% NaCl,  $C_{14-15}$ -8PO-SO<sub>4</sub>Na/2-butanol/7w/v% NaCl and  $C_{14-15}$ -8PO-SO<sub>4</sub>Na/1-octanol/4w/v% NaCl. It was found that  $S^*_{new}$  decreased from 8w/v% NaCl for no alcohol to 7w/v% NaCl for 90 mM 2-butanol and 4w/v% NaCl for 90 mM 1-octanol as shown in Fig. 2.5. At optimum salinity, the maximum cold water detergency of solid coconut oil increased from  $62.1 \pm 3.9\%$  removal with no added salt to  $95.4 \pm 0.2\%$  removal in 0.1w/v%  $C_{14-15}$ -8PO-SO<sub>4</sub>Na/90 mM 1-octanol/4w/v% NaCl at 10°C. Now that the surfactant/alcohol system has been optimized for salinity, the octanol concentration was reevaluated by varying 1-octanol concentration using  $S^*_{new}$  (4w/v% NaCl) in the surfactant formulation as shown in Fig. 2.6. It was observed that octanol concentration could be decreased from 1.17w/v% (90 mM) to as low as 0.2w/v% with minimal effect on detergency performance (i.e., cold water detergency results still exceeding 90%). It is worth noting that in this our final optimized system (0.1w/v%  $C_{14-15}$ -8PO-SO<sub>4</sub>Na/0.2w/v% 1-octanol/4w/v% NaCl), the alcohol and surfactant are present at a similar concentration (within a factor of 2). While admittedly the salt concentration in this system is high for detergency purposes, in past research we have demonstrated the ability to adjust the surfactant system design to reduce the salinity value to reasonable levels (Attaphong & Sabatini, 2017).

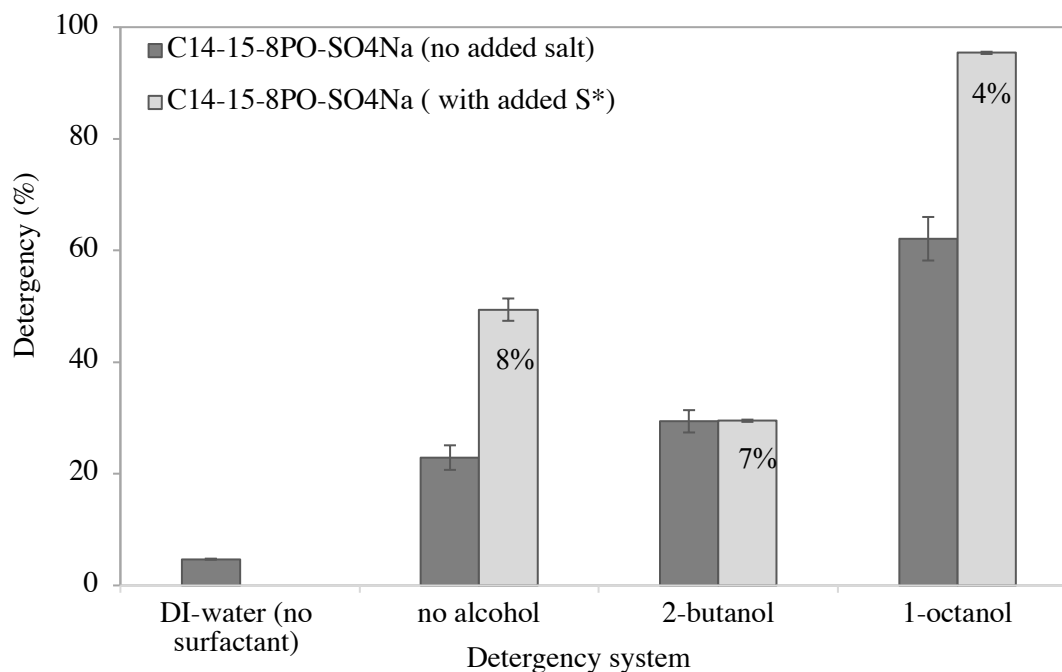


Figure 2.5 Cold water detergency performance of coconut oil in different 0.1 w/v% C<sub>14-15-8PO-SO<sub>4</sub>Na/90 mM alcohol (when present) systems at a washing temperature of 10°C</sub>

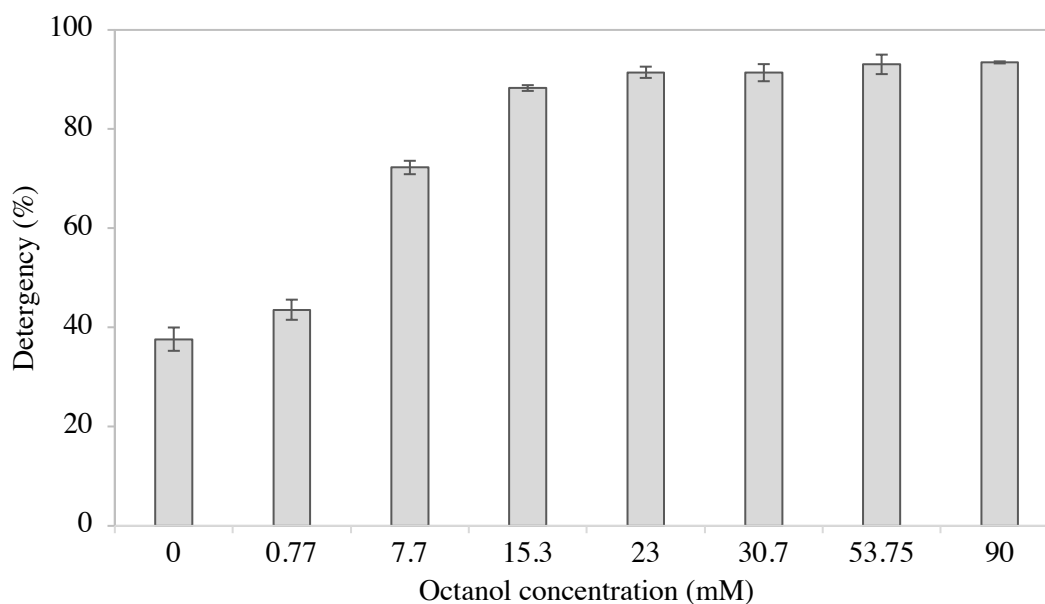


Figure 2.6 Effect of varying 1-octanol concentration in 0.1 w/v% C<sub>14-15-8PO-SO<sub>4</sub>Na at 4 w/v% NaCl on cold water detergency of coconut oil</sub>

### *Mean particle size and zeta potential measurements of the optimized surfactant solutions*

Table 2.4 presents the mean coconut soil particle size suspended during detergency studies and the corresponding solid particle zeta potentials in the wash solutions at two different times (day 1 and day 8). The maximum cold water detergency of the optimized system (C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na/1-octano/4w/v% NaCl) showed the largest removed solid particle sizes (1.25±0.20 for day 1 and 1.10±0.08 for day 8), while, for the washing system with DI-water, the removed particles were the smallest (0.02±0.00 for day 1 and 0.17±0.01 for day 8). These results vary from those of Chanwattanakit et al. (2017) where smaller soil particles were observed in the higher detergency systems; reasons for this variation in observations are not clear at this time. Anti-redeposition is one of required laundry processes for inhibiting the dislocated soil particles to reattach the fabric during the laundry process. This mechanism can be explained by dispersion stability. Therefore, zeta potential measurements of the detached coconut semisolid particles in washing solutions were carried out. Table 2.4 shows the zeta potential of different wash solutions for two different periods of time at 10°C. It was observed that when the sole anionic surfactant system was used in the wash step, the zeta potential of coconut soil particles became more negative than DI-water due to anionic surfactant adsorption. When salt and alcohols were introduced to the anionic surfactant formulations, the zeta potential dramatically decreased (less negative). This is due to the fact that counterions increase ionic strength resulting in compression of the double layer next to the adsorbed surface layer (Gu & Li, 1997). However, the decreased dispersion stability in the presence of alcohols can be attributed to the anions of anionic surfactant in the Stern layer were replaced by the neutral charge of alcohol resulting in a lowering of Stern potential ( $\Psi_s$ ) and decreased the stability (Dan et al., 2009). Although, the presence of both salt and alcohols decreased zeta potential of the suspended soil particles in the washing solutions, the soil particles for all studied surfactant formulations were still stable colloids over time because colloidal particles with zeta potential values greater than 20 mV typically have high degrees of dispersion stability (Tadros, 2015). These results suggested that good dispersion stability is not a responsible mechanism to explain the improved cold water detergency observed in this work.

Table 2.4 Mean coconut solid particle sizes, zeta potentials and detergency of coconut oil at 10°C in different washing baths

Detergency system	Mean solid particle size ( $\mu\text{m}$ )		Zeta potential (mV)		Detergency (%)
	Day 1	Day 8	Day 1	Day 8	
DI-water	0.02 $\pm$ 0.00	0.17 $\pm$ 0.01	-47.4 $\pm$ 3.89	-49.5 $\pm$ 2.96	4.7 $\pm$ 0.1
C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na	0.17 $\pm$ 0.01	0.15 $\pm$ 0.02	-137.6 $\pm$ 1.01	-109.2 $\pm$ 8.31	22.9 $\pm$ 2.2
C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na/ 8w/v% NaCl	0.28 $\pm$ 0.02	0.26 $\pm$ 0.01	-32.3 $\pm$ 2.15	-42.1 $\pm$ 2.00	49.4 $\pm$ 2.0
C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na/ 2-butanol/7w/v% NaCl	0.17 $\pm$ 0.01	0.14 $\pm$ 0.01	-21.6 $\pm$ 2.12	-35.8 $\pm$ 7.99	29.4 $\pm$ 0.2
C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na/ 1-octanol/4w/v% NaCl	1.25 $\pm$ 0.20	1.10 $\pm$ 0.08	-32.2 $\pm$ 9.23	-43.5 $\pm$ 6.05	95.4 $\pm$ 0.2

## Conclusions

Cold water detergency of triacylglycerol semisolid soils is a complicated process. Surfactant-alcohol adsorptions (wetting) were primarily required to prepare for loosening (penetration) the soil molecules, followed by solubilization-emulsification to remove the soils from the fabric. The key findings obtained from this study are summarized as follows;

- 1) The maximum cold water detergency was achieved when intermediate-chain alcohols (1-heptanol (C7) or 1-octanol (C8)) were introduced and the optimum salinity was adjusted to account for the alcohol ( $S^*_{\text{new}}$ ) in the detergency system.
- 2) Good cold water detergency of solid coconut oil corresponded to lower values of IFT and contact angle.
- 3) Intermediate-chain alcohols (1-heptanol, 1-octanol or 1-nonanol) enhanced cold water detergency for all three surfactant systems and both soil systems studied, demonstrating robustness in this approach.
- 4) A decrease in melting point of the soil and dispersion stability of the removed solid particles

was not observed to play a significant role on the increased cold water detergency observed in this research.

5) Solid coconut oil removal over 90% was achieved in 0.1w/v% C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na/0.2w/v% 1-octanol/4w/v% NaCl at 10°C- a very encouraging result.

Future research will focus on the effect of varying surfactant structures (alkyl chain length, number of PO, number of EO and type of head group) and alcohol structures (linear and branched chains) on cold water detergency of coconut oil. In addition, the mixtures of triacylglycerol soil with different chain lengths and unsaturation will be conducted to investigate the impact of varying semisolid soil on cold water detergency.

### **Acknowledgements**

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## Chapter 3 The effect of surfactant systems, alcohol types and salinity on cold-water detergency of triacylglycerol semisolid soil. Part II

### Abstract

Our prior work found that detergency of coconut oil was relatively poor using C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na alone but showed promising improvement with the presence of linear intermediate-chain alcohols (C7-C9 alcohols) in the surfactant formulation. The maximum detergency exceeded 90% removal using 0.1 w/v% C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na/0.2 w/v% 1-octanol/4 w/v% NaCl (final optimized surfactant system) at 10°C. The current work thus seeks to further investigate surfactant formulations capable of providing improved detergency performance. Different 50% linear anionic extended surfactant structures (LC<sub>14-15</sub>-8PO-SO<sub>4</sub>Na, LC<sub>14-15</sub>-8PO-3EO-SO<sub>4</sub>Na, and LC<sub>14-15</sub>-8PO-7EO-SO<sub>4</sub>Na) were compared with the branched C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na previously studied. Detergency of coconut oil using C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na at 8 w/v% NaCl (S\*) still performed more effectively than these new surfactant systems. The addition of octanol as a detergency additive was further studied, and it showed that S\* reduced from 8 w/v% NaCl to 4 w/v% NaCl for 1-octanol and to 2 w/v% NaCl for 2-octanol and 2-ethyl-hexanol in the C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na surfactant formulation. Coconut oil removal significantly improved from roughly 49% for no alcohol with 8 w/v% NaCl, to 83% for 2-ethyl-hexanol with 2 w/v% NaCl, to 95% for 1-octanol with 4 w/v% NaCl, and to 98% for 2-octanol with 2 w/v% NaCl. Further studies on octanol concentration showed that decreasing 1-octanol from 1.2% (90 mM) to 0.2% (15.3 mM) and 2-octanol from 1.2% (90 mM) to 0.5% (38.5 mM) still maintained detergency over 90% removal. In this work, cold water detergency was found to correlate with low IFT above the melting point, improved wetting of the semisolid soil, and oil solubilization in surfactant micelles.

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- 2) Phaodee, P., & Sabatini, D. A. (2020) The effect of surfactant systems, alcohol types, and salinity on cold water detergency of triacylglycerol semisolid. Part II. *Journal of Surfactants and Detergents*, 23:423-432.



## Introduction

Cold-water detergency of triacylglycerol semisolid soils is challenging because triacylglycerols are massive molecules composed of a glycerol bound to three fatty acid molecules. The glycerol portion of the molecule is polar, while the long fatty-acid alkyl chains are hydrophobic. Currently, the household laundry detergency trend is towards lower washing temperatures. Under these conditions, many triacylglycerol soils behave as semisolid soils which contain both solid and liquid triacylglycerol matrices (Timms, 1985) with the liquid portion being entrapped in the crystalline solid fat portion (Chanwattanakit et al., 2017b). These combined properties limit the ability of surfactants to penetrate into the soil, resulting in even poorer detergency performance than for hydrocarbon solid soils and fatty acids.

Semisolid soil removal is a complex process involving multiple removal mechanisms (Cox, 1986). Previous work has evaluated detergency removal mechanisms of triacylglycerol semisolid soils at washing temperatures below their melting points using a range of surfactants (Beaudoin et al., 1995; Cox et al., 1987; Scheuing, 1990; Shaeiwitz et al., 1981). Surfactant-water penetration was found to be an important process whereby surfactants and water diffused into the solid soil to modify the microstructure and promote liquefaction or softening of the soil. In combination with the applied agitation force, this could break off parts of the swollen soil and disperse them into the washing bath due to the surfactant-induced decline in cohesive forces within the soil matrix. Using a Fourier transform infrared spectroscopy (FT-IR) technique, Scheuing (1990) found that tristearin was removed through the penetration of surfactant and water into the tristearin, causing the formation of a liquid crystalline phase at the interface between the soil and surfactant solution. This process then allowed the soil to be removed through surfactant-based emulsification-solubilization (Cox, 1986). Chanwattanakit et al. (2017) found that a majority of the removed methyl palmitate was found in free-semisolid forms, which were dispersed and floated in the washing bath along with a small amount of solubilized soil in surfactant micelles. The detergency system should therefore be maximized to attain optimum soil removal by optimizing surfactant-water and surfactant-soil interactions.

Surfactants have been used as one of the active components in laundry detergents because they can reduce surface tension, interfacial tension (IFT), and also increase the wettability of the

substrate surface, thereby enhancing the cleaning process (Charoensaeng et al., 2008; Kalak and Cierpiszewski, 2015; Rosen and Kunjappu, 2004; Witthayapanyanon et al., 2010). Anionic surfactants have been widely used in cleaning applications due to temperature insensitivity (Velásquez et al., 2010). Recently, novel anionic surfactants have been synthesized to improve properties of conventional surfactants with the intermediate addition of ethylene oxide (EO) groups and propylene oxide (PO) groups. Anionic surfactants with the intermediate insertion of PO and EO groups are known as anionic extended surfactants which further increase surfactant-soil interaction with the insertion of PO groups and surfactant-water interaction with the insertion of EO groups. An important advantage of anionic extended surfactants over conventional surfactants is their ability to achieve higher solubilization capacity and ultralow IFT ( $<10^{-3}$  mNm<sup>-1</sup>) with vegetable oils (Do and Sabatini, 2010; Miñana-Perez et al., 1995; Phan et al., 2010), which have been shown to be critical in the detergency process. Chanwattanakit et al. (2017) found that the cold-water detergency of methyl palmitate, the semisolid soil used in their study, was about 25% removal at 15°C and 30% removal at 20°C using 0.1 wt% C<sub>12-13</sub>-4PO-SO<sub>4</sub>Na at 5 wt% NaCl. Similarly, our previous work (Phaodee et al., 2018) reported that cold water detergency of coconut oil was approximately 20% removal using 0.1 w/v% C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na alone and 50% removal using C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na at 8 w/v% NaCl (S\*) which was found to demonstrate the lowest IFT. These prior results demonstrate that cold water detergency of semisolid soils using a single surfactant alone is often inadequate.

Alcohols have been widely used as surfactant additives in many industries; (e.g., enhanced oil recovery (EOR), pharmaceuticals, and detergency (Krüssmann and Bercovici, 1991; McKarns et al., 1997; Sabatini et al., 2003)). Acosta et al. (2003) found that adding 90 mM oleyl alcohol (long-chain alcohol) and 180 mM sodium mono and dimethyl naphthalene sulfonate (SMDNS) to a 4 w/v% sodium bis(2-ethyl)dihexyl sulfosuccinate (AOT) with 5 w/v% NaCl formulation improved motor oil removal efficiency from approximately 30% to over 85%. Thus, alcohols have proved to be a valuable additive in surfactant formulations with the role of the alcohol being a function of the alkyl chain length (Graciaa et al., 1993; Salager et al., 2005). Intermediate- to long-chain alcohols (i.e., octanol) have been shown to partition to the oil-water interface near the surfactant tail at sufficient concentrations (sometimes referred to as lipophilic linkers) and have an increased interaction with the polar oil molecule thereby altering the nature of the oil-water interface and

effectively decreasing the apparent carbon number of the oil (decreasing hydrophobicity of oil) (Kahlweit et al., 1990; Salager et al., 2019). The decreasing relative hydrophobicity of the oil with the presence of lipophilic linker required lower  $S^*$  to attain the optimum surfactant formulation where a minimum IFT and maximum solubilization were achieved (Acosta et al., 2003; Graciaa et al., Lachaise et al., 1993; Sabatini et al., 2003; Salager et al., 1979; Salager et al., 2019). Evidence has shown that this behavior correlates with detergency of semisolid triacylglycerol soils as well (Mankowich, 1963; Phaodee et al., 2019).

Our prior work attempted to introduce a series of alcohols in the  $C_{14-15}$ -8PO- $SO_4Na$  surfactant formulation to study the effect of alkyl chain length on detergency of coconut oil and palm kernel oil. The results showed that the alcohols with intermediate-chain lengths (C7-C9 alcohols) showed greater detergency improvement than did shorter- (C4 and C6 alcohols) and longer-chain alcohols (C10 alcohol) in the surfactant formulation. Further, the intermediate-chain alcohols performed best for a range of surfactants;  $C_{14-15}$ -8PO- $SO_4Na$  (anionic extended surfactant),  $C_{10-16}$ -7EO-OH (alcohol ethoxylate surfactant), and  $C_{10}$ -18PO-2EO- $SO_4Na$  and dioctyl sodium sulfosuccinate (SDOSS) at 0.26/0.74 mole fraction (mixture of anionic surfactant), corresponding to lower IFT above the melting point and higher wetting (Phaodee et al., 2018). This is in agreement with results of Graciaa et al. (1993) who reported C6-C10 alcohols adsorbed near the surfactant tail and provided extra interaction with the oil, thus demonstrating stronger surfactant-soil interaction and enhanced oil solubilization capacity, whereas shorter- and longer-chain alcohols behaved differently.

Hence, this current work aims to extend our previous work by attempting to further explore surfactant formulations capable of providing good cold-water detergency of coconut oil. The effects of anionic extended surfactant structure (e.g., branching degree and number of EO groups) and use of branched octanols (2-octanol and 1-ethyl-hexanol) on detergency performance of semisolid coconut oil were studied. In addition, IFT above coconut oil melting's point, contact angle measurements, and oil solubilization studies were evaluated.

## Experimental Procedures

### *Materials*

Coconut oil (*cocos nucifera*, reported melting point = 27.5°C (Phaodee et al., 2018)) and octanols (1-octanol, 2-octanol, and 2-ethyl-hexanol) were all purchased from Sigma Aldrich (St. Louis, MO, USA). The anionic extended surfactants evaluated in this study, summarized in Table 3.1, were provided by Sasol North America, Inc. (Lake Charles, LA, USA). Sodium chloride (NaCl) with 99% purity was purchased from Avantor Performance Materials, Inc. (Center Valley, PA, USA). Blended 65/35 polyester/cotton (3×4 inch in size) was purchased from Test Fabrics, Inc. (West Pittston, PA, USA). All materials and chemicals were used without further purification.

Table 3.1 Properties of anionic extended surfactants and octanols

Nomenclature	Degree of linearity (%)	%active	Molecular weight (MW, g /mole)	Melting point (°C)
<u>Surfactants</u>				
C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na	0	93.84	787	-
LC <sub>14-15</sub> -8PO-SO <sub>4</sub> Na	50	86.4	787	-
LC <sub>14-15</sub> -8PO-3EO-SO <sub>4</sub> Na	50	25.0	919	-
LC <sub>14-15</sub> -8PO-7EO-SO <sub>4</sub> Na	50	25.0	1095	-
<u>Octanols</u>				
1-octanol		98.0	130.23	-15
2-octanol		97.0	130.23	-38
2-ethyl-hexanol		99.6+	1302.3	-76

### *Methodology*

#### *Dynamic Interfacial (IFT) Measurement*

Dynamic IFT experiments were conducted to determine the IFT between the surfactant

formulations and melted coconut oil at 30°C (above the melting point) using a spinning drop tensiometer purchased from the University of Texas (Model 500). A volume of 1-3  $\mu\text{L}$  melted coconut oil was injected into a 300- $\mu\text{L}$  capillary tube which was filled with a surfactant solution having different NaCl concentrations and octanol types. Surfactant and octanol concentrations were kept constant at 0.1w/v% and 90 mM, respectively. The oil drop radius was recorded for 20 minutes after oil injection corresponding to the washing cycle length in detergency experiments. The IFT was calculated using the following equation given by Vonnegut (1942),

$$\gamma = \frac{(\rho_1 - \rho_2)\omega^2 R^3}{4}$$

where  $\rho_1 - \rho_2$  is the difference in densities between the heavy and light phases,  $\omega$  is angular velocity (radius/second) and R is the radius of the cylindrical drop, as measured in the instrument.

#### *Detergency Experiments*

##### *Soiling Procedure*

Detergency studies were carried out using 3×4in.-zig zagged swatches of blended 65/35 polyester/cotton. Coconut oil was heated to 30°C (above its melting point) and mixed at 20% by volume chloroform. The swatches were completely submerged in the oil/chloroform solution for one minute and hung to dry overnight in a fume hood prior to use. All swatches were freshly prepared with the average weight ratio of coconut oil : fabric approximately 0.23 ± 0.01:1 g.

##### *Detergency Procedure*

Detergency experiments were carried out using a Terg-O-Tometer (Model 7243; USA Testing Co., Inc., Hoboken, NJ). A 20-minute wash cycle was performed with 1 L surfactant solution, followed by a 3-minute first rinse and a 2-minute second rinse with 1 L DI-water (Phan et al., 2010; Tanthakit et al., 2010). Washing and rinsing cycles were performed at about 120 rpm agitation speed. The bath temperature was kept constant at 10°C during the washing and rinsing steps. After the rinse cycles were complete, the washed fabrics were removed and dried by hanging overnight using one wooden clothespin per fabric. The detergency was determined by dividing the mass of removed soil after wash to the mass of initial oil soiled. All laundry experiments were repeated in triplicate and the error bars presented in the detergency results are standard deviations.

### *Contact Angle Measurement*

Measurement of the contact angle through surfactant droplet was measured after 30 seconds at ambient temperature of  $20 \pm 2^\circ\text{C}$  (Chanwattanakit et al., 2017). The contact angle was carried out by the sessile drop method using an optical tensiometer (Biolin Scientific). An aliquot of approximately  $2 \mu\text{L}$  of the surfactant solution containing the same solutions as those of the selected washing solutions was dropped on the solid coconut oil coated on the fabric using a micro-syringe. The fabric samples with coated coconut oil were dried in a fume hood for 24 hours before use which was identical to the soiling procedure in detergency experiments. All contact angle measurements were repeated in triplicate and the error bars presented in the contact angle results are standard deviations.

### *Oil Solubilization Study*

Selected surfactant solutions were freshly prepared and an excess amount of solid coconut oil was then added in the surfactant solutions. This experiment was conducted for 20 minutes at 120 rpm and  $10^\circ\text{C}$  using a Terg-O-Tometer to simulate oil solubilization capacity in the detergency experiments (Chanwattanakit et al., 2017). After 20 minutes, the surfactant mixtures containing solubilized coconut oil in the surfactant solution and excess solid coconut oil were filtered through 0.2-micron filter papers. The filtrates were diluted to measure the amount of oil solubilization based on total organic carbon (TOC) content using a Multi N/C 2100S analyzer (Analytik Jena, Jena, Germany). The amount of solubilized coconut oil was calculated by subtracting the TOC value of surfactant and solubilized coconut oil (post solubilization study) with the TOC value of surfactant alone. All solubilization studies were repeated in triplicate.

## **Results and Discussion**

### ***Effect of linear chain and number of EO of surfactant on IFT and $S^*$***

Different  $\text{C}_{14-15}\text{-8PO-SO}_4\text{Na}$  based-surfactant structures were evaluated for their detergency performance;  $\text{C}_{14-15}\text{-8PO-SO}_4\text{Na}$  (previously studied),  $\text{LC}_{14-15}\text{-8PO-SO}_4\text{Na}$ ,  $\text{LC}_{14-15}\text{-8PO-3EO-SO}_4\text{Na}$ , and  $\text{LC}_{14-15}\text{-8PO-7EO-SO}_4\text{Na}$ . The IFT and  $S^*$  results for these surfactants and coconut oil are shown in Fig. 3.1. Comparing the effect of branched chain on  $S^*$ ,  $S^*$  increased slightly from

8 w/v% NaCl for C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na to 9 w/v% NaCl for LC<sub>14-15</sub>-8PO-SO<sub>4</sub>Na. The minimum IFT value (at S\*) of C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na was slightly lower than that of LC<sub>14-15</sub>-8PO-SO<sub>4</sub>Na. Previous research indicated that increased branching could form larger aggregates (bilayer or vesicles) which favored middle phase microemulsion formation and ultralow IFT with triacylglycerol soils (Phan et al., 2011). The results in Fig. 3.1 also show that S\* increased with the presence of EO groups in the 50% linear chain surfactants (13 w/v% with the presence of 3(EOs) and 16 w/v% with the presence of 7(EOs)). These results demonstrated that higher degrees of ethoxylation (EO groups) increases the hydrophilicity of the surfactant system, thus requiring higher S\* to obtain optimum surfactant formulation (Phan et al., 2011). In addition, the insertion of EO group in the 50% linear surfactants tended to increase minimum IFT values which is undesirable for detergency.

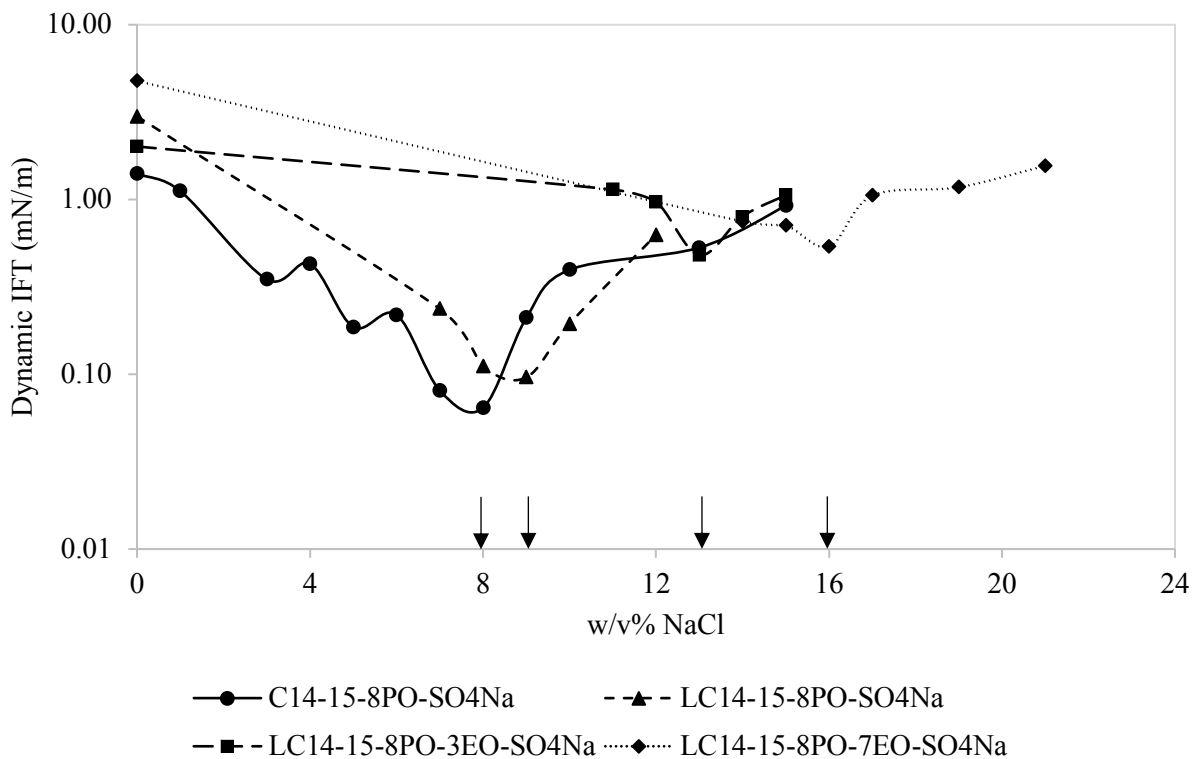


Figure 3.1 IFT between coconut oil and different anionic extended surfactant systems through dynamic IFT measurement at 30°C. The minimum IFT of each surfactant corresponds to its S\* as denoted by ↓. All surfactant concentrations were constant at 0.1 w/v%.

### ***Detergency of coconut oil using various surfactant systems without and with added salt at S\****

Previous studies have demonstrated that detergency performance can be affected by surfactant structure (Kabin et al., 1998; Kanasaki et al., 2016; Tanthakit et al., 2010; Weerawardena et al., 2000). This current work thus attempts to further explore the efficacy of anionic extended surfactant structures (e.g. linear versus branching and number of EO groups) on removal efficiency as presented in Fig. 3.2. The detergency of coconut oil at 10°C increased with the presence of S\* in all surfactant systems studied. Interestingly, coconut oil removal using previously studied C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na without and with added salt at S\* was still better than those of the new surfactant systems evaluated. The maximum coconut oil removal was approximately 49% using the C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na at 8 w/v% (S\*) (Fig. 3.2) corresponding to the lowest minimum IFT (IFT = 0.06 mNm<sup>-1</sup>) (Fig. 3.1). For the 50% linearity surfactants, even though the minimum IFT was below < 1 mN/m range (Fig. 3.1), which has been shown to be a desired IFT range for detergency of various soils (Attaphong and Sabatini, 2017; Phaodee et al., 2018; Tongcumpou et al., 2003), the detergency performance was still much lower than for the branched C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na surfactant. There is an evidence that branched-extended surfactant with the insertion of PO group showed lower IFT, thus better detergency (Fig. 3.2). However, these results demonstrated that IFT alone did not capture the entirety of the detergency behavior using different C<sub>14-15</sub>PO<sub>8</sub>SO<sub>4</sub>Na propoxylated structures varying degrees of linearity and ethoxylation. Other mechanisms (e.g., wetting and solubilization) should be further considered.



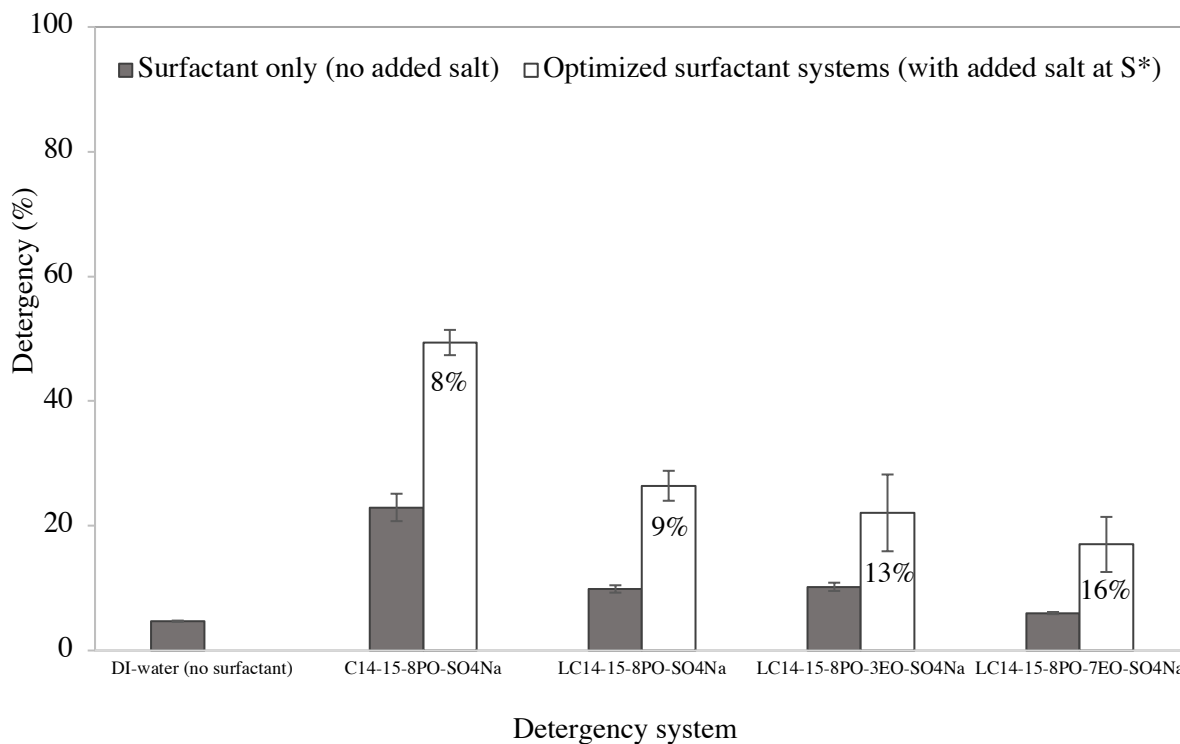


Figure 3.2 Cold water detergency of coconut oil using different anionic extended surfactant systems at 10°C. All surfactant concentrations were constant at 0.1 w/v%. Numbers indicate in the figure are S\* for each surfactant formulation.

### ***Effect of octanol type on S\****

Since the previously studied C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na showed better coconut oil removal than other surfactant systems studied, the effect of branched octanols on detergency performance was next studied with the C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na surfactant. Studies previously found that alcohols modify properties of microemulsion systems including relative hydrophilicity, oil solubilization, coalescence rate, and the rigidity of the interface (Acosta et al., 2003b; Lim et al., 1992). The modification in relative hydrophilicity suggested that S\* might require adjustment for the alcohol being considered. Salager et al. (1979) found that a change in S\* associated with the alcohol type. The IFT measurement at 30°C was therefore conducted to determine adjusted S\* with the presence of octanol in the surfactant formulation. Results in Fig. 3.3 demonstrate that adding linear octanol (1-octanol) as previously studied decreases the S\* from 8 to 4 w/v% NaCl. Interestingly, the

addition of branched octanols further decreased  $S^*$  to 2 w/v% NaCl for both 2-octanol and 2-ethyl-hexanol. The decrease in  $S^*$  with these alcohols is attributed to the evidence that the alcohols altered the composition of the oil interface, which decreased the effective carbon number of the interface (Kahlweit et al., 1990) and thus reducing the  $S^*$  required (Kahlweit et al., 1990; Salager et al., 2013). The IFT results showed that the addition of 1-octanol or 2-octanol to the surfactant systems reduced the minimum IFTs (at  $S^*$ ) to as low as  $0.03 \text{ mNm}^{-1}$  which was even lower than that of  $\text{C}_{14-15}\text{-8PO-SO}_4\text{Na}$  at 8 w/v% NaCl studied before ( $0.06 \text{ mNm}^{-1}$ ).

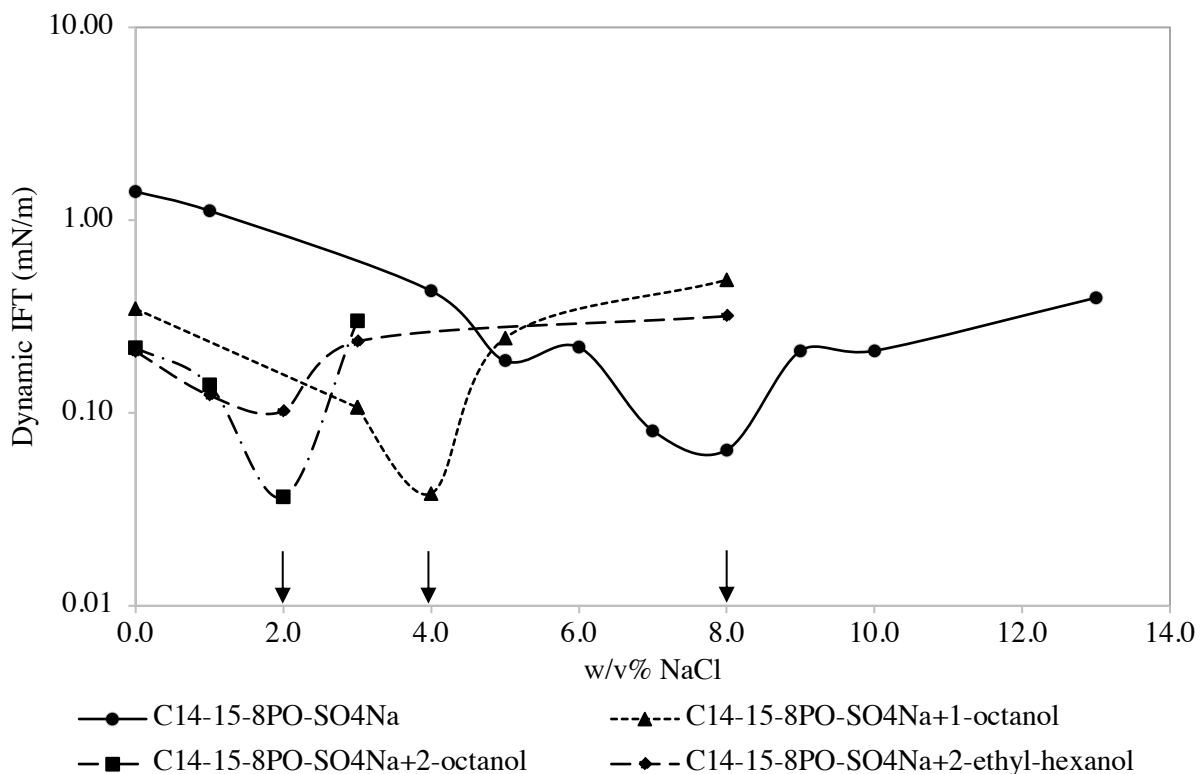


Figure 3.3 IFT between coconut oil and  $\text{C}_{14-15}\text{-8PO-SO}_4\text{Na}$  with added different octanol types through dynamic IFT measurement at  $30^\circ\text{C}$ . The minimum in IFT of each surfactant corresponds to its  $S^*$  as denoted by  $\downarrow$ . Surfactant and octanol concentrations were constant at 0.1 w/v% and 90 mM, respectively.

#### *Effect of octanol type on coconut oil removal*

Figure 3.4 presents coconut oil removal using various surfactant formulations without and with added salt at  $S^*$ . The results show that coconut oil removal using DI-water only achieved 5%

removal. When surfactant was introduced in the washing bath, improved detergency was attained (49% removal for C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na at 8 w/v% NaCl). However, the detergency is still below desirable levels. The addition of 1-octanol in the surfactant system was studied in previous work and exhibited significant improvement in detergency (approximately 60% removal without salt and over 95% removal with 4 w/v% NaCl (S\*)). In this work, branched octanols (2-octanol and 2-ethyl-hexanol) as detergency additives were explored to evaluate detergency of coconut oil with C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na. In the absence of salt, the addition of 2-octanol or 2-ethyl-hexanol in the C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na further enhanced detergency performance, exceeding 80% removal compared to approximately 60% removal using 1-octanol (Fig. 3.4). In the presence of adjusted S\*, detergency performance further improved to over 95% removal using the surfactant systems with added 1-octanol (95.5 ± 0.2% removal) or 2-octanol (98.3 ± 2.4% removal) but not with added 2-ethyl-hexanol (83.0 ± 3.0% removal). Exploring this further, 1-octanol or 2-octanol with added salt at S\* lowered IFT by almost an order of magnitude, while this lower IFT was not observed for 2-ethyl-hexanol (Fig. 3.3). It should be further noted that over 95% coconut oil removal was observed with IFTs of 0.03 mNm<sup>-1</sup> or higher, suggesting that ultralow IFT (10<sup>-3</sup> mNm<sup>-1</sup>) was not required for good coconut oil removal. The results in Figs 3.3 and 3.4 also revealed that the minimum IFTs of optimized surfactant formulations were in the same IFT range, but the detergency was significantly improved with the addition of octanol in the surfactant system, suggesting that mechanisms beyond IFT reduction are necessary to explain the alcohol effect on detergency improvement.

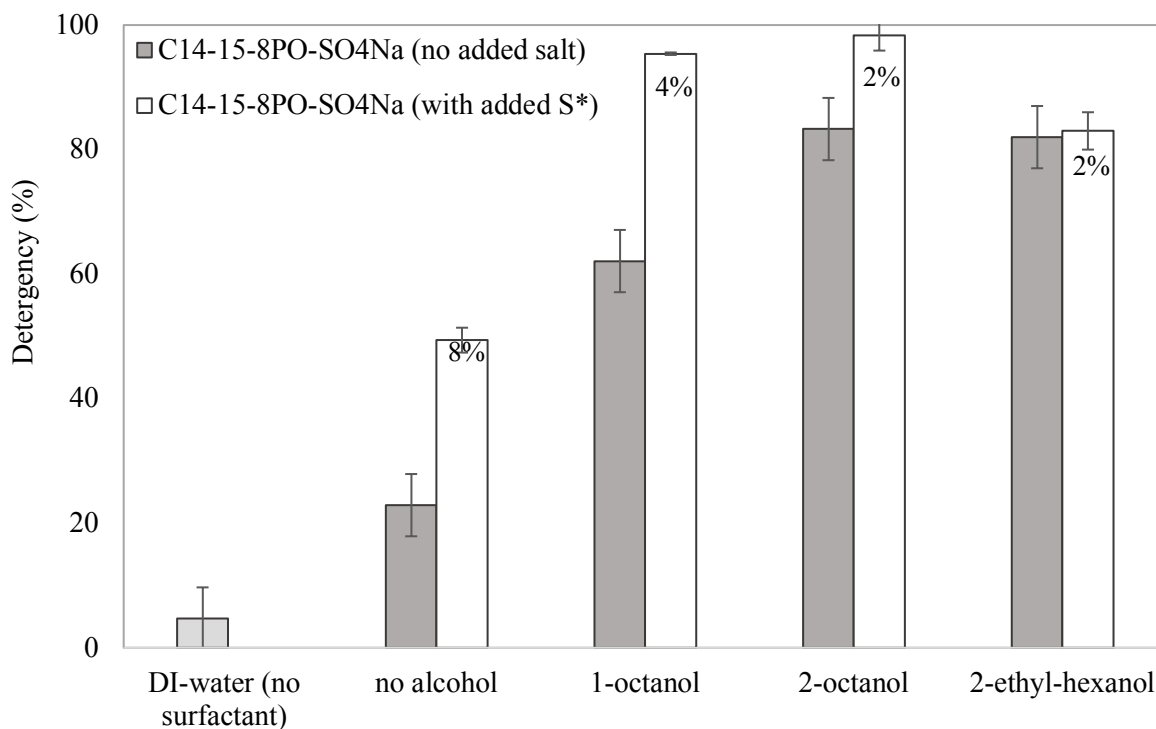


Figure 3.4 Cold water detergency of coconut oil using C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with added various octanol types at 10°C. Surfactant and octanol concentrations were constant at 0.1 w/v% and 90 mM, respectively. Numbers indicate in the figure are S\* for each surfactant formulation.

### ***Correlation between detergency and contact angle***

Previous research has demonstrated a correlation between detergency and contact angle for semisolid soils. The improved detergency of semisolid soils is attributed to surfactant-water penetration; higher penetration of surfactant solution (better wetting) has been shown to correlate with lower contact angle (Rosen and Kunjappu, 2004). Figure 3.5 illustrates the correlation between detergency and contact angle of various optimized surfactant formulations. Using a C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na at 8 w/v% NaCl system showed high contact angle (70°) indicating that the semisolid coconut oil was poorly wet by the surfactant-water system corresponding to low detergency of 49.4 ± 2.0% removal. In contrast, the contact angles at 20°C of C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na/1-octanol at 4 w/v% NaCl and C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na/2-octanol at 2 w/v% NaCl systems were 34.3° ± 0.2° and 32.9° ± 1.2°, respectively corresponding to detergency over 95% removal, whereas

contact angle of C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na/2-ethyl-hexanol at 2 w/v% NaCl was higher ( $42.6^\circ \pm 2.5^\circ$ ) presenting 83% removal. These results suggested that higher detergency corresponded to lower contact angle and thus better wetting. Previous research has suggested that improved wetting could be a potential mechanism to improve detergency and thus be used in design of optimized detergency systems for semisolid soils (Chanwattanakit et al., 2017b; Kalak and Cierpiszewski, 2015). The possible reason why detergency with added 2-ethyl-hexanol and salt at S\* was not as high as those of 1-octanol and 2-octanol is hypothesized to be that 2-ethyl-hexanol, which has only six carbons on a linear chain, did not penetrate into the solid coconut oil molecule as deep as those of 1-octanol or 2-octanol which have eight carbons on the linear chain; the poorer surfactant penetration is hypothesized to cause higher contact angle (Fig. 3.5) as well as poorer detergency.

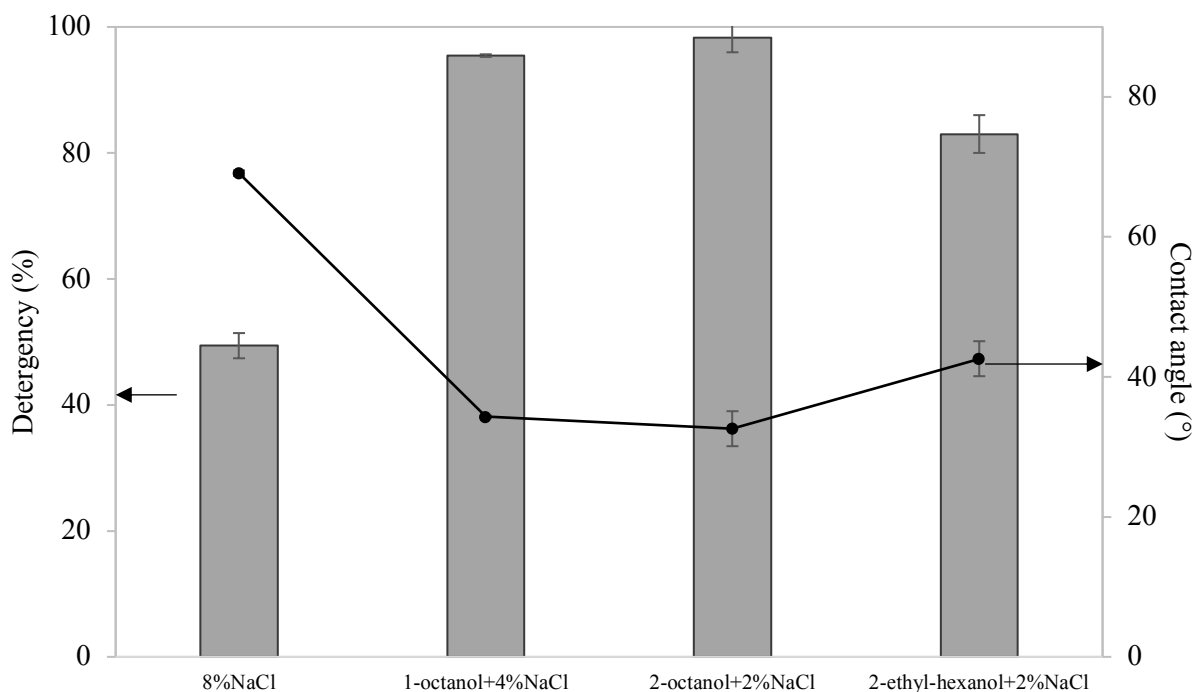


Figure 3.5 Correlation between detergency and contact angle of various optimized surfactant systems. Surfactant and octanol concentrations were 0.1. w/v% and 90 mM, respectively.

### ***Correlation between detergency and solubilization***

Past research has shown that improved detergency of semisolid soils was correlated to higher solubilization by surfactant micelles (Cui et al., 2012; Miller and Raney, 1993). Results of coconut

oil solubilization capacity in different optimized surfactant formulations in our research are summarized in Table 3.2. The experiment was carried out at 10°C to simulate oil solubilization in the washing bath. The results indicated that the optimized surfactant formulations with added octanols increased oil solubilization from 13 mg/L (no alcohols) to approximately 53 mg/L with an increase in detergency from around 49% to over 95% removal, respectively. Our results were consistent with Chanwattanakit et al. (2017) showing that methyl palmitate removal using C<sub>12-13</sub>-4PO-SO<sub>4</sub>Na was increased from roughly 40 to 70 % at 20°C with increased oil solubilization from approximately 21 to 23.5 mg/L. While, detergency was shown to improve with increasing solubilization, on a mass basis only a small amount of solubilized soil was observed in the washing solution. In our work, approximately 690 mg of solid coconut oil was coated on the polyester/cotton fabrics in 1 L surfactant solution. The maximum solubilized oil was 53.89 mg/L as listed in Table 3.2. The percentage of soil solubilized is calculated to be only 8% of the total amount of removed soil (98% removal of the 690 mg added soil). Our results are in a good agreement with previous work (Kabin et al., 1996) who observed that around 10% of abietic acid (highly viscous liquid soil) was removed into nonionic surfactant micelles for 4 hours of contacting time using a quartz crystal microbalance (QCM) technique. Rather than being solubilized, a significant portion of removed semisolid soil was dislodged from the fabric as solid particles by surfactant penetration which is consistent with results of Scott (1963). Thus, improved solubilization and semisolid dispersion appear to be correlated.

Table 3.2 Oil solubilization study

Surfactant systems	Oil solubilization (mg/L)
0.1%C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na+8w/v%NaCl	13.08 ± 1.21
0.1%C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na+90mM 1-octanol+4%NaCl	52.12 ± 0.85
0.1%C <sub>14-15</sub> -8PO-SO <sub>4</sub> Na+90mM 2-octanol+2%NaCl	53.89 ± 3.61

***Comparing optimal concentration of 1-octanol and 2-octanol in C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na formulations***

Based on past research, octanol concentrations have thus far been held constant at 90 mM (1.17 w/v%) as a reference system for the all detergency experiments. We now study the impact of lower

octanol concentrations in the surfactant formulations. Two detergency formulations ( $C_{14-15}$ -8PO-SO<sub>4</sub>Na/1-octanol/4 w/v% NaCl and  $C_{14-15}$ -8PO-SO<sub>4</sub>Na/2-octanol/2 w/v% NaCl) demonstrating superior detergency performance were selected to examine the impact of varying octanol concentrations on detergency. As depicted in Fig. 3.6, the detergency reached a plateau at 0.2 w/v% (15.3 mM) for 1-octanol and 0.5 w/v% (38.5 mM) for 2-octanol. Further, the optimized detergency performance still exceeded 90% removal. These studies demonstrated that using linear octanol required higher S\* and lower concentration than branched octanols suggesting that there is a trade-off between using linear and branched alcohol. Currently, the reasons why 2-octanol requires higher concentrations than 1-octanol is not well understood and should be evaluated in further research.

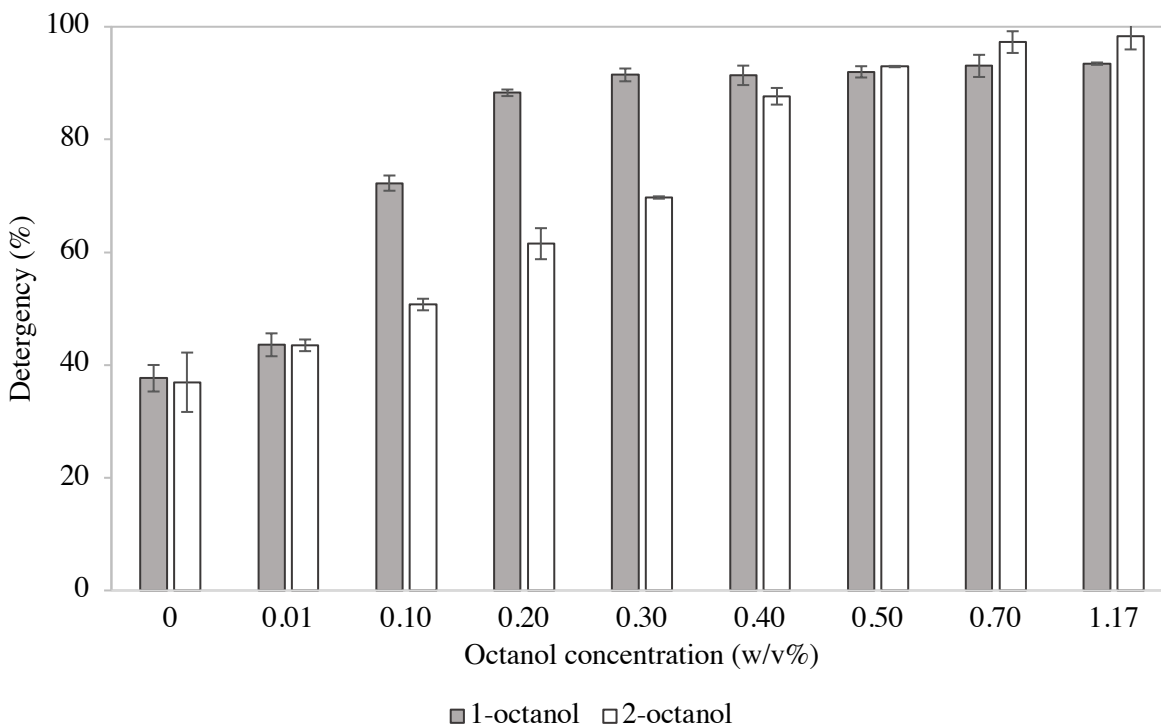


Figure 3.6 The effect of varying additive concentrations on cold-water detergency of coconut oil at 10°C. Surfactant concentration was kept constant at 0.1 w/v%.

## Conclusions

This work extended our prior research focused on surfactant formulations, providing optimum cold-water detergency of semisolid coconut oil. Using new surfactant systems ( $\text{LC}_{14-15}\text{-8PO-SO}_4\text{Na}$ ,  $\text{LC}_{14-15}\text{-8PO-3EO-SO}_4\text{Na}$ , and  $\text{LC}_{14-15}\text{-8PO-7EO-SO}_4\text{Na}$ ) did not show higher coconut oil removal than  $\text{C}_{14-15}\text{-8PO-SO}_4\text{Na}$  previously studied, demonstrating that increased linearity and EO groups did not improve detergency. In the presence of octanol in  $\text{C}_{14-15}\text{-8PO-SO}_4\text{Na}$  systems, the  $S^*$  decreased from 8 w/v% for no added octanols to 4 w/v% for 1-octanol and to 2 w/v% for both 2-octanol and 2-ethyl-hexanol. Improved detergency exceeding 90% removal was observed using the  $\text{C}_{14-15}\text{-8PO-SO}_4\text{Na}$  formulations with added 1-octanol or 2-octanol and salt at its  $S^*$ . Further, decreasing 1-octanol and 2-octanol concentrations from 1.17 w% (90 mM) to 0.2% (15.3 mM) and to 0.5% (38.5 mM), respectively, still achieved high detergency performance (over 90% removal). In this work, improved cold-water detergency of coconut oil was correlated with bath-soil surface modification (i.e., wetting and IFT reduction) and oil solubilization in surfactant micelles in the bulk aqueous solution. This research thus supports the addition of intermediate-chain alcohols as a promising additive to achieve desired cold-water detergency of triacylglycerol semisolid soils. Future work will study the effect of surfactant concentration on cold-water detergency of coconut oil and employ the hydrophilic-lipophilic deviation (HLD) to predict detergency for a variety of soils.

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## Chapter 4 Correlation between detergency of different oily and solid non-particulate soils and hydrophilic-lipophilic deviation (HLD)

### Abstract

This research examined the correlation between the detergency of soils with varying equivalent alkane carbon numbers (EACNs) and hydrophilic-lipophilic deviation (HLD) values. The detergency of oily soils with EACNs ranging from 5.2 to 16.6 was evaluated using C<sub>10</sub>-4PO-SO<sub>4</sub>Na as a primary surfactant system and a 1:1 binary mixture of C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT as a confirmatory surfactant system (with 65/35 polyester/cotton at 25°C). These surfactant systems were characterized using HLD concepts which showed that C<sub>10</sub>-4PO-SO<sub>4</sub>Na was more hydrophilic (had a higher negative C<sub>c</sub> value) than that of the mixed surfactant system. Detergency of the selected soils was evaluated at different salinities corresponding to HLDs ranging from negative to positive values. The results showed that detergency of all soils increased with increasing salinity (starting with an HLD = -3.0 (Winsor Type I microemulsion), reached the maximum at widely different optimum salinity (S\*) but at an identical HLD value of zero (optimum Type III), and then decreased with further increasing salt levels corresponding to positive HLD values (Type II). The preferred HLD range from -3.0 to 0.0 showed detergency levels exceeding 80% removal with interfacial tension values (IFTs) below 1 mNm<sup>-1</sup> for all oily soils studied. Detergency of octadecane (EACN = 18, solid at 25°C) was further conducted and demonstrated that performing detergency at HLD = -3.0 to 0.0 likewise revealed superior soil removal (over 80%) versus systems with HLD values outside this range. Thus, this work highlighted the utility of using the HLD approach in designing surfactant formulations for detergency of soils with widely varying EACNs.

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- 3) Phaodee, P., Harwell J. H., & Sabatini, D. A Correlation between detergency of different oily and solid non-particulate soils and hydrophilic-lipophilic deviation (HLD) accepted in Journal of Surfactants and Detergents, May 27<sup>th</sup> 2020.

## Introduction

Surfactants are a major component of laundry detergents, being as high as 15 - 40% of the total detergency formulation (Scheibel, 2004). Surfactants, in particular anionic surfactants, have been extensively utilized to remove soils such as motor oil, liquid triglycerides (cooking oils), and semisolid triglycerides (butters) from fabrics. The dominant removal mechanisms of oily soil removal have been demonstrated to be rollup and snap-off (emulsification-solubilization) (Miller and Raney, 1993; Tongcumpou et al., 2005). In general, surfactant molecules adsorb on the oil-bath interface and reduce the role of cohesion, thereby facilitating the oil droplet detachment from itself on the fabric surface. These mechanisms are facilitated by the low interfacial tension (IFT) between the oil and the washing bath (surfactant solution) and the mechanical energy from the agitation cycle (Childs et al., 2005; Rosen and Kunjappu, 2004; Tongcumpou et al., 2005). In contrast, the removal mechanism for solid non-particulate soils has been shown to be different from oily soils. Penetration of surfactant and water into the solid soil matrix has been considered as a primary mechanism, thereby disordering or liquefying of the solid soil to facilitate the soils displacement from the fabric surface (Chanwattanakit et al., 2017; Cox, 1986; Cox et al., 1987; Phaodee et al., 2019; Scheuing and Hsieh, 1988).

Microemulsions are thermodynamically stable mixtures of oil, water, and surfactant and are typically classified into four types. A Winsor Type I microemulsion has oil solubilized in normal micelles within the water phase. In a Winsor Type II microemulsion, however, surfactant-solubilized water exists in reverse micelles within the oil phase. In a Winsor Type III microemulsion, also referred to as a middle phase microemulsion, surfactant, oil, and water are solubilized in the middle phase with the excess oil and water phases in equilibrium with the middle phase. When the middle phase volume increases and becomes a single phase with increasing surfactant concentration, it is known as a Winsor Type IV microemulsion. Microemulsion phase behavior transitions from Winsor Type I, to Type III and to Type II (hydrophilic to hydrophobic systems) with increasing salinity level for ionic surfactants and temperature for nonionic surfactants (Rosen and Kunjappu, 2004). Previous work has determined the relationship between microemulsion type and detergency and found that microemulsion phase behavior impacts detergency (Do et al., 2015; Tongcumpou et al., 2003). Excellent detergency of motor oil was

observed with decreasing IFT using a surfactant system in the Type I region but close to a Type III microemulsion, and at the optimum Type III microemulsion (optimum salinity ( $S^*$ ) (Tongcumpou et al., 2003). The detergency results showed that the mixed surfactant system required different salinity ranges for soils with varying hydrophobicity (5 – 8% NaCl for hexadecane (EACN = 16) and 12 - 16 % NaCl for motor oil (EACN = 23.5)) to attain good soil removal (Tongcumpou et al., 2003). In studying detergency of canola oil (EACN = 17) using different surfactant formulations, the maximum removal was observed at 14% NaCl using  $C_{14-15}$ -8PO-SO<sub>4</sub>Na (Phan et al., 2010), whereas Do et al. (2015) found the maximum detergency at  $S^*$  of 2.5 w/v% NaCl using a binary surfactant mixture of  $C_{10-18}$ PO-2EO-SO<sub>4</sub>Na and dioctyl sodium sulfosuccinate (AOT) at 26:74 molar ratio. The optimum surfactant formulation ( $S^*$ ) is thus observed to be influenced by the hydrophilic/hydrophobic nature of the surfactant system and the EACN of the oil.

Although the correlation between detergency and microemulsion phase behavior has been extensively studied, the correlation between detergency and hydrophilic-lipophilic deviation (HLD) has not been studied systematically. Thus, the motivation of the current work is to utilize the HLD concept for evaluating detergency of soils with widely varying equivalent alkane carbon numbers (EACNs) at different surfactant-system HLD values. In this work,  $C_{10-4}$ PO-SO<sub>4</sub>Na was selected as the primary surfactant based on previous work (Budhathoki et al., 2016), which showed that it could form a middle phase microemulsion with varying-EACN oils. The binary surfactant mixture of  $C_{10-4}$ PO-SO<sub>4</sub>Na and AOT was also investigated as a confirmatory system to demonstrate the optimum HLD range for a second detergency system. Detergency of five different oily soils with different hydrophobic/hydrophilic natures were evaluated; 1) Soygold1100 (SG1100) and canola oil mixture at 1:1 by volume, 2) isopropyl myristate (IPM), 3) SG1100 and canola oil mixture at 2:3 by volume, 4) IPM and canola oil mixture at 1:1 by volume, and 5) hexadecane and canola oil mixture at 1:1 by volume, all at 25°C. In addition, IFT measurements were conducted to examine its correlation with detergency. Lastly, detergency of octadecane (EACN = 18, solid non-particulate soil at 25°C) was performed to evaluate if the optimum HLD found for oily soils can be employed for a solid non-particulate soil as well.

As stated in the objective, the current work aims to demonstrate a correlation between detergency of widely varying EACNs of soils and surfactant-system HLD values. The HLD equation was first



proposed by Salager et al. (1979) to describe microemulsion phase behavior. The HLD value indicates the deviation of the surfactant formulation from the optimum condition ( $S^*$ ) (Acosta et al., 2008; Budhathoki et al., 2016; Zarate-Munoz et al., 2016) where an equal amount of water and oil are solubilized in the middle phase, the coalescence rate is fastest, the IFT is minimum (denoted as  $IFT^*$ ), and the solubilization capacity (SP) is highest ( $SP^*$ ). Negative, zero, and positive values of HLD correspond to Winsor Type I, III and II microemulsions, respectively. Two HLD equations exist depending on the nature of the surfactant head group; ionic surfactants and nonionic surfactants. Since all surfactants used in this work are anionic surfactants, the appropriate HLD equation for anionic surfactants is described below

$$HLD = \ln(S) - K \times EACN - f(A) - \alpha\Delta T + Cc \quad (4.1)$$

Where S is salinity of the aqueous phase (g NaCl/100 mL), K is a function of anionic surfactant head group and is reported to range from 0.004 - 0.17 (Acosta et al., 2008; Hammond and Acosta, 2012; Salager et al., 1979; Velásquez et al., 2010; Witthayapanyanon et al., 2008). EACN is the equivalent alkane carbon number describing the hydrophobic/hydrophilic nature of the oil; for example, hexane has an ACN (EACN) of 6 and canola oil has an EACN of 17 (Do et al., 2009). The hydrophobicity of oil increases with increasing EACN.  $f(A)$  is a function of alcohol or cosolvent, if present, and depends on the alcohol type and concentration.  $\alpha$  is the temperature coefficient (typically is  $0.01 \text{ K}^{-1}$  for most surfactants (Broze, 1999; Hammond and Acosta, 2012; Salager et al., 1979)).  $\Delta T$  is the difference between the studied temperature and reference temperature ( $T-25^\circ\text{C}$ ). The Cc value describes the relative hydrophilic/lipophilic nature of the surfactant. A negative Cc value corresponds to a hydrophilic surfactant which preferably forms normal micelles in the aqueous phase. In contrast, a positive Cc corresponds to a hydrophobic surfactant which favors the formation of reverse micelle in oil phase (Acosta et al., 2012; Witthayapanyanon et al., 2008).

A salt scan is performed to attain the optimum formulation ( $S^*$ ) for ionic surfactants. If the optimum condition ( $S^*$ ) is obtained without alcohol ( $f(A) = 0$ ), and at  $25^\circ\text{C}$  ( $\Delta T = 0$ ), the HLD is equal to 0 ( $HLD = 0$ ) and the general HLD equation can be rewritten as shown below

$$\ln(S^*) = K \times EACN - Cc \quad (4.2)$$

In order to obtain K and Cc values of a studied surfactant system, microemulsion phase behavior studies of reference oils (known EACNs) are conducted to determine S\* to construct a linear plot of ln(S\*) against EACN. From the plot, K and negative Cc are the slope and y-intercept of that studied surfactant, respectively.

## **Experimental Procedures**

### ***Materials***

The anionic extended surfactant studied in this work, C<sub>10</sub>-4PO-SO<sub>4</sub>Na (28% purity), was supplied by Sasol North America, Inc. (Lake Charles, LA, USA). The C<sub>10</sub>-4PO-SO<sub>4</sub>Na is a commercial grade surfactant which is a polydisperse mixture of a variety of EO group with a mole average of 4 EO groups – it should be noted that the surfactant characteristics (K and Cc values) can be influenced by surfactant polydispersity. The anionic conventional surfactant studied, a waxy solid dioctyl sodium sulfosuccinate (Aerosol OT (AOT)), 100% purity), was purchased from Fisher Scientific. Hexane, octane, decane, dodecane, hexadecane, octadecane, and isopropyl myristate (IPM) were all purchased from Sigma Aldrich (St. Louis, MO, USA). Canola oil was purchased from a local grocery store. Soygold 1100 (SG1100), which is a methyl soyate, was received from Ag Processing Inc. (APG) (Omaha, NE, USA). Blended 65/35 polyester/cotton swatches (3×4 inch in size) were purchased from Test Fabrics, Inc. (West Pittston, PA, USA). All materials and chemicals were used without further purification.

### ***Methodology***

#### ***Microemulsion phase behavior studies***

Microemulsion phase studies of all studied oils were performed in 15 mL flat-bottom vials with Teflon-lined screw caps. Five milliliters of 2 w/v% surfactant in aqueous phase were prepared at different salinities, then 5 mL of studied oil was added in the vial to obtain an aqueous surfactant solution-to-oil volumetric ratio of unity. All vials containing the mixtures were mixed well by hand once a day for 3 days and placed in a temperature-controlled water bath at 25°C. The S\* was visually observed and determined after simultaneously shaking all the vials in the phase scan. The

surfactant formulation with shortest coalescence time for each set of phase scan was defined as the  $S^*$  (Budhathoki et al., 2016; Zarate-Munoz et al., 2016).

#### *Dynamic IFT Measurements*

Dynamic IFT measurements were performed to determine the IFT between the surfactant formulations and the oil and to confirm  $S^*$  obtained through the microemulsion phase study. The IFT experiments were carried out using a spinning drop tensiometer purchased from the University of Texas (Model 500). A volume of 1-3  $\mu\text{L}$  studied oil was injected into a 300  $\mu\text{L}$  capillary tube filled with a freshly prepared surfactant solution for 20 minutes at 25°C after oil injection corresponding to the washing timeframe in detergency experiments. The surfactant formulation with the lowest IFT was defined as the optimum formulation ( $S^*$ ).

#### *Detergency Experiments*

##### *Soiling Procedure*

Detergency experiments were performed using 3×4-inch swatches of blended 65/35 polyester/cotton. All studied oily soils were mixed at 20 vol% chloroform whereas octadecane (reported melting point obtained from the manufacturer = 26 - 29°C) was heated to 35°C before mixing with chloroform. The swatches were completely soaked in the oil/chloroform solution for 1 minute, then the soiled swatches were hung using one wooden clothespin per fabric to dry and allowed chloroform evaporate off overnight in a fume hood prior to use (Do et al., 2015).

##### *Detergency Procedure*

Detergency experiments were carried out at  $25 \pm 1^\circ\text{C}$  using a Terg-O-Tometer (Model 7243; USA Testing Co., Inc., Hoboken, NJ, USA). A 20-min wash cycle was performed for washing with 1 L surfactant solution. A 3-min first rinse and a 2-min second rinse were performed with one L of deionized (DI) water. The agitation speed during washing and rinsing cycles was approximately 120 rpm. The bath temperature was kept constant during the washing and rinsing steps. After the rinse cycles were complete, washed fabrics were then hung using a wooden clothespin to dry overnight in a fume hood. The detergency performance was determined gravimetrically by weighing the pre-soiled, soiled and washed fabrics directly on the mass scale as per past research (Do et al., 2015; Attapong and Sabatini, 2017). The percentage of oil removal was determined by

dividing the mass of removed soil after wash by the mass of initial oil soiled and multiplied by 100. All laundry experiments were repeated in triplicate and the error bars presented in the detergency results represent standard deviations.

## **Results and Discussion**

### ***Determinations of K and Cc-values for studied surfactant systems***

Microemulsion phase behavior studies were conducted at 25°C with five paraffinic oils (hexane, octane, decane, dodecane, and hexadecane which have respective EACN values of 6, 8, 10, 12, and 16) to determine surfactant characteristics (K and Cc values) using the HLD equation for ionic surfactants. The optimum salinities (S\*) of the selected oils were first determined using 2 w/v% surfactant concentration (C<sub>10</sub>-4PO-SO<sub>4</sub>Na and a binary mixture of C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio) as identified in Table 4.1. From Table 4.1, it can be observed that the S\* of both surfactant systems increased with increasing EACN of the oil. The S\* determined for each surfactant system with five different EACNs of oils were then used to construct a graph of ln(S\*) against EACN as presented in Fig. 4.1. The results showed the R<sup>2</sup> value of linear fitting for both surfactant systems studied was 0.97 suggesting that the linear fit was in very good agreement with the data. According to eq. 4.2, the slope of the linear plot fit to this data is the K-value and the y-intercept is the negative Cc value for the respective surfactant systems. Results in Fig. 4.1 suggest that the K and Cc values for C<sub>10</sub>-4PO-SO<sub>4</sub>Na surfactant were 0.053 and -2.29, respectively, which is consistent with previous work by Budhathoki et al. (2016) who reported K and Cc values of 0.069 and -2.15, respectively, for the same surfactant. The K and Cc values for the C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT mixture were found to be 0.090 and -0.80, respectively. The Cc values for these surfactant systems studied suggest that the single C<sub>10</sub>-4PO-SO<sub>4</sub>Na surfactant system was more hydrophilic than the C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT mixture; this was as expected as the AOT is a more hydrophobic surfactant.

Table 4.1 S\* for each studied oil using different surfactant systems

Paraffinic oils	EACN	C <sub>10</sub> -4PO-SO <sub>4</sub> Na		C <sub>10</sub> -4PO-SO <sub>4</sub> Na+AOT at 1:1 by molar ratio	
		S* (w/v%)	ln(S*)	S* (w/v%)	ln(S*)
Hexane	6	13.0	2.56	3.5	1.26
Octane	8	15.3	2.73	4.8	1.58
Decane	10	17.5	2.86	5.7	1.73
Dodecane	12	18.6	2.93	7.0	1.94
Hexadecane	16	22.4	3.11	9.0	2.19

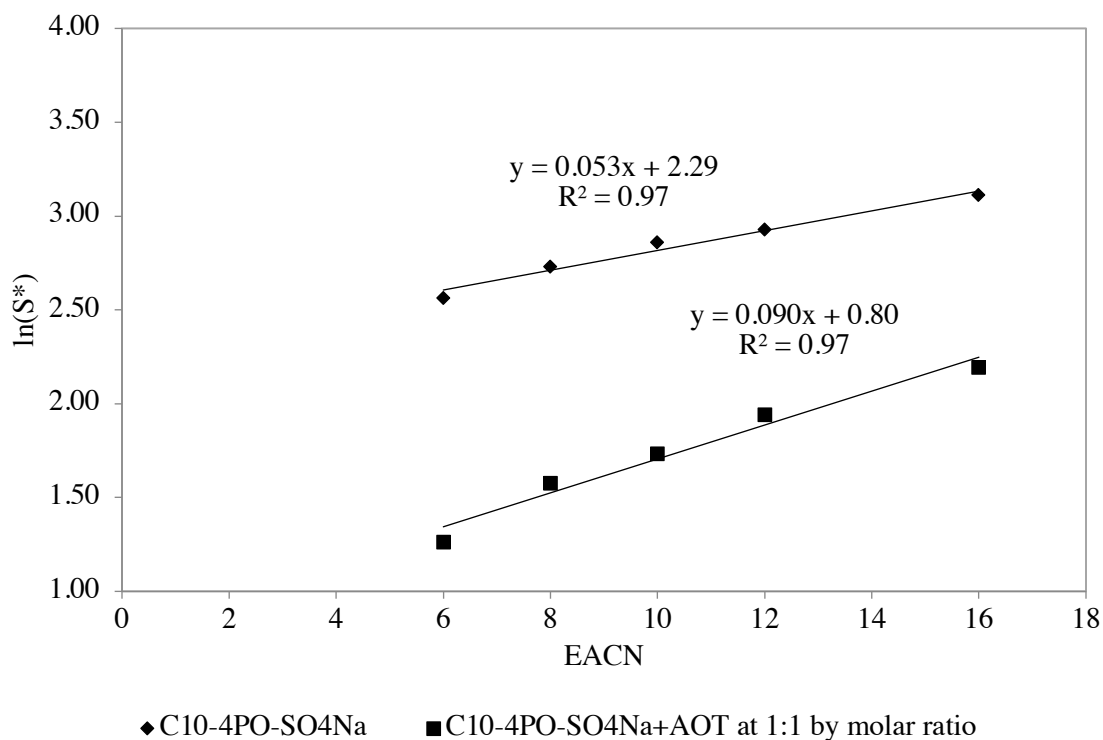


Figure 4.1 Plot of ln(S\*) against EACN to determine surfactant characteristics (K and C<sub>c</sub> values) for studied surfactant systems

***Determination of EACNs of studied oils for detergency study***

In this work, five different soils were studied consisting of a variety of oils with different EACN values (while initially the plan was to study varying ratios of a binary triglyceride mixture, forming

middle phase microemulsions with these systems proved to be problematic). Before studying detergency of the five soils, the  $S^*$  of each soil was determined using the  $C_{10}$ -4PO- $SO_4Na$  surfactant as a primary surfactant using microemulsion phase behavior studies at 25°C. In addition, the  $S^*$  and  $IFT^*$  between the oil and surfactant were then determined through dynamic IFT measurement at 25°C as a confirmatory step, as shown in Table 4.2. The microemulsion phase behavior results showed that middle phase microemulsion was visually observed using 2%  $C_{10}$ -4PO- $SO_4Na$  for all oils studied. Their coalescence rates varied from 30 seconds to several minutes (all fairly rapid) depending on the molecular structure of oil and mixing ratio. The slowest coalescence rate was observed with the oil mixture having the highest canola oil ratio. Furthermore,  $S^*$  for a mixture of 1:1 v/v hexadecane and canola oil (EACN = 16.6) from phase behavior studies, for example, was observed to be 23.8% w/v NaCl which was identical to  $S^*$  based on IFT results. Results in Table 4.2 show that the  $S^*$  obtained through the IFT measurements varied from 13.0 w/v% NaCl for the mixture of SG1100 and canola oil at 1:1 by volume to 23.8 w/v% NaCl for the mixture of hexadecane and canola oil at 1:1 by volume. Further, the  $IFTs^*$  for the studied soils were all observed to be in the ultralow IFT range ( $10^{-3}$  mNm<sup>-1</sup>) which corroborates the presence of middle phase microemulsions in the phase behavior studies. The EACN of each soil was then determined using eq. 4.2 where the  $S^*$  and HLD parameters ( $K = 0.053$  and  $C_c = -2.29$ ) for the  $C_{10}$ -4PO- $SO_4Na$  surfactant were known. The EACNs of the soils were found to vary from 5.2 to 16.6 suggesting that the latter was most hydrophobic, based on its highest EACN value in this work.

Table 4.2  $S^*$  based on IFT measurements,  $IFT^*$ , and calculated EACNs for all five oils studied

Studied oils	$S^*$ (w/v%)	$IFT^*$ (mNm <sup>-1</sup> )	EACN ( $\ln(S^*) = 0.053 \times EACN + 2.29$ )
1:1 v/v SG1100+canola oil	13.0	$2.0 \times 10^{-3}$	5.2
Isopropyl myristate (IPM)	14.7	$1.1 \times 10^{-3}$	7.5
2:3 v/v SG1100+canola oil	16.9	$2.0 \times 10^{-3}$	10.1
1:1v/v IPM+canola oil	19.5	$2.7 \times 10^{-3}$	12.8
1:1v/v hexadecane+canola oil	23.8	$3.3 \times 10^{-3}$	16.6

***Detergency results: Correlation between detergency of soils, salinity, HLD and IFT using C<sub>10</sub>-4PO-SO<sub>4</sub>Na surfactant as a primary surfactant study***

The detergency of the five oily soils was measured with 65/35 polyester/cotton blend and at a washing temperature of 25°C. The detergency was evaluated at different salinities corresponding to HLD values varying from negative to zero to positive (Type I, III and II microemulsions, respectively) as shown in Fig. 4.2a-e. Detergency of SG1100 and canola oil mixture at 1:1 by volume (EACN = 5.2), for example, significantly increased at 0.1 w/v% NaCl with an IFT value of 0.7 mNm<sup>-1</sup> corresponding to HLD = -5.0, plateaued at NaCl concentrations between 0.2 w/v% with an IFT value of 0.3 mNm<sup>-1</sup> and 13.0 w/v% (S\*) with a minimum IFT value (IFT\*) of 2.0×10<sup>-3</sup> mNm<sup>-1</sup> corresponding to HLDs ranging from -4.0 to 0.0, and then declined at NaCl concentrations greater than 13.0 w/v% corresponding to HLDs > 0.0 and with IFT values > IFT\*. The maximum oil removal for EACN = 5.2 (>90% removal) was observed at 13.0 w/v% NaCl (S\*) corresponding to the HLD = 0.0 formulation with IFT\* of 2.0×10<sup>-3</sup> mNm<sup>-1</sup>, as shown in Fig. 4.2a. The correlation between detergency, HLD and IFT was found to follow a similar trend for the other soils studied (Fig. 4.2b-e).

In general, the correlation between detergency of studied soils and salinity demonstrated that detergency increased with increasing salinity levels, reached the maximum at its S\* (over 90% removal), then decreased at salinity levels higher than the S\* with significant drop in detergency at salt concentrations further away from the S\*. The S\* was found to increase with increasing EACNs of the soil (S\* varied from 13 w/v% NaCl for EACN = 5.2 to 23.8 w/v% for EACN = 16.6). It is especially interesting to note that good detergency (>80% removal) was observed in widely varying salt concentration ranges (i.e., 0.2 - 13.0 w/v% NaCl for EACN = 5.2 and 0.4 - 23.8 w/v% NaCl for EACN = 16.6 (Fig. 4.2a and 4.2e)) suggesting that different salinity ranges are required for detergency of soils with varying EACN values.

The correlation between detergency and IFT demonstrated increased detergency corresponding to lower IFT values. Improved detergency (>80% removal) could be achieved with IFT values in the 0.1 to 1.0 mNm<sup>-1</sup> range for all studied soil systems. Further, maximum detergency was correlated with the attainment of IFT\* values which were found to be in an ultralow IFT range (<10<sup>-2</sup> mNm<sup>-1</sup>) for all soils studied as depicted in Fig. 4.2a-e. Attaphong and Sabatini (2017) found good

detergency of canola oil (approximately 80% removal) using anionic extended surfactant with Type I formulation at an IFT value between 0.1 and 1.0 mNm<sup>-1</sup>. Likewise, Thompson (1994) also showed that maximum detergency occurred near the S\* for an anionic surfactant with triolein. Similar results could be observed in other studies (Tanthakit et al., 2010; Tongcumpou et al., 2005). It was worth noting that IFT < 1 mNm<sup>-1</sup> appeared to be sufficiently low to facilitate oil detachment by rollup and snap-off mechanisms with the introduction of agitation force during the detergency process (Attaphong and Sabatini, 2017; Tongcumpou et al., 2005). Therefore, the attainment of ultralow IFT (< 10<sup>-2</sup> mNm<sup>-1</sup>) is not necessary to achieve good detergency (defined here as > 80% removal) of oily soils.

Subsequently, studied salt concentrations were converted to HLD values using the HLD eq. (K and Cc values for C<sub>10</sub>-4PO-SO<sub>4</sub>Na). The detergency of all studied soils at HLDs varying from negative to positive (Type I, III, and II microemulsions) is also demonstrated in Fig. 4.2a-e. Increased detergency was achieved with increasing HLD values from negative to zero (Type I to optimum Type III microemulsions) and maximum detergency was observed in the vicinity of HLD = 0. These results were in good agreement with previous studies (Do et al., 2015; Tongcumpou et al., 2005) that found increasing oil removal efficiency as the microemulsion phase approached the optimum Type III region (HLD = 0). Improved detergency of oily soils had been observed in Type I/III microemulsion boundary system (HLD approaching 0) where the IFT was relatively low (< 1 mNm<sup>-1</sup>), thereby favoring rollup and snap-off mechanisms and resulting in superior oil removal efficiency (Acosta et al., 2003; Thompson 1994; Tongcumpou et al., 2003; Wu et al., 2000). A reduction in detergency was found when detergency was conducted at a salinity value above the optimum formulation (HLDs > 0) suggesting that a Type I approaching to a Type III surfactant formulation (HLD ≤ 0) is the preferred region for detergency. In this research, we were unable to systematically study the effect of oily soil structure on detergency vs HLD – this should be evaluated in future research.



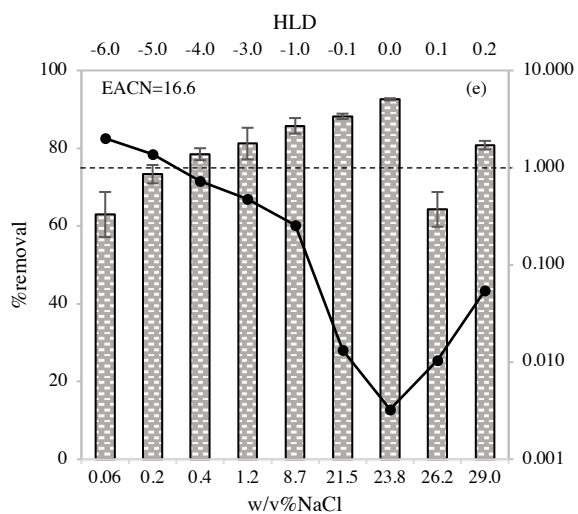
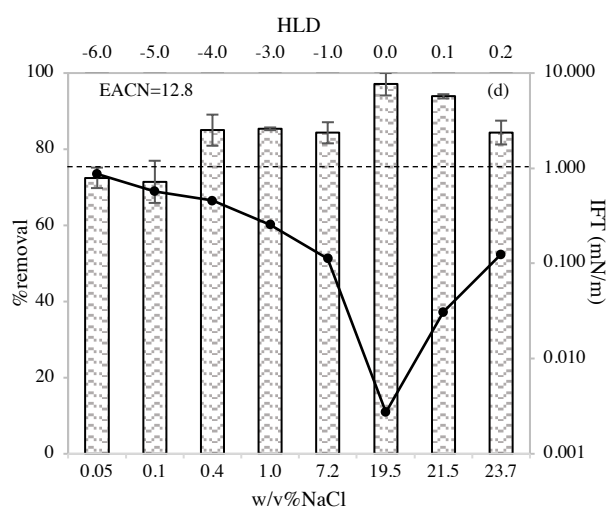
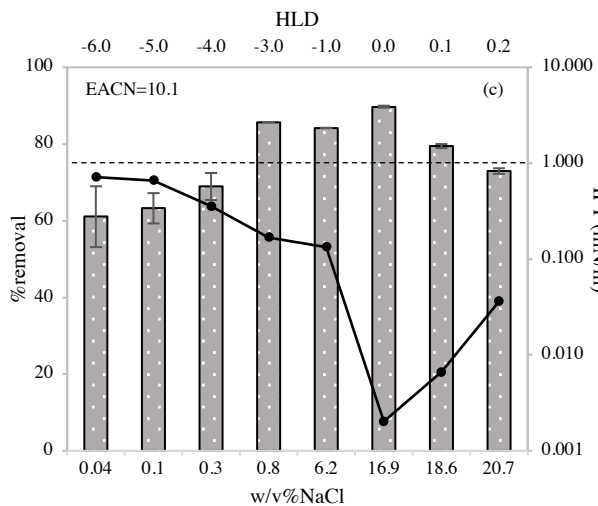
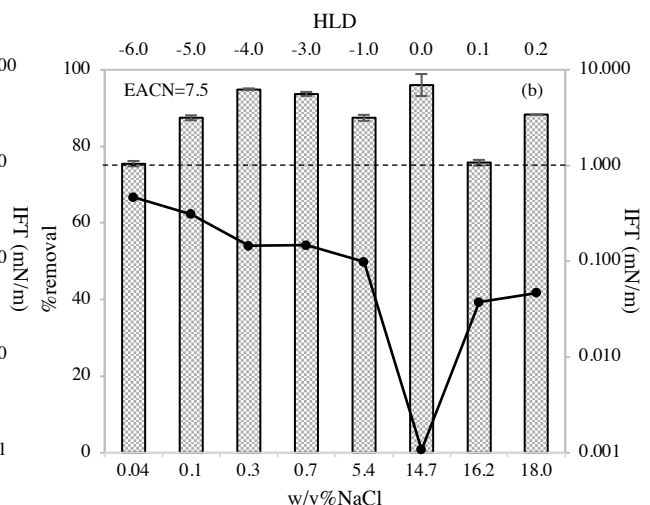
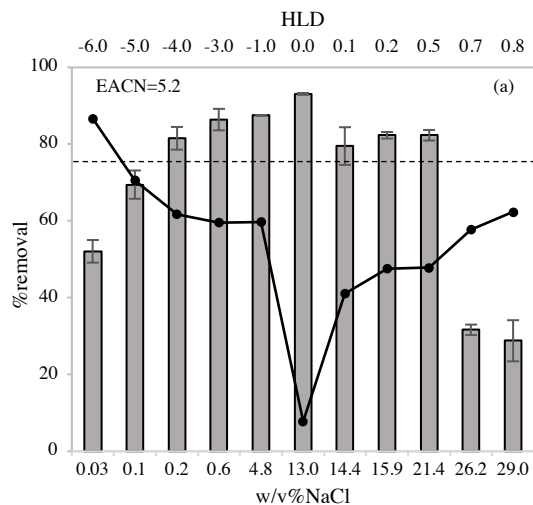


Figure 4.2 Correlation between detergency, salinity, HLD, and IFT for different EACNs of studied soils. **a)** EACN = 5.2, **b)** f EACN = 7.5, **c)** EACN =10.1, **d)** EACN =12.8, and **e)** EACN = 16.6. Detergency studies (bar charts) and dynamic IFT measurements (line charts) were all conducted using 0.1 w/v% C<sub>10</sub>-4PO-SO<sub>4</sub>Na at 25 ± 1°C. The horizontal dash lines indicate IFT with 1 mNm<sup>-1</sup>.

### ***Correlation between detergency and HLD***

Fig. 4.3 presents the combined detergency results of all studied soils with respect to system HLD values varying from negative to positive. The high positive HLD values (i.e., HLDs = 0.5, 0.7, and 0.8) could not be performed for the higher EACN oils due to the solubility limit of NaCl for the C<sub>10</sub>-4PO-SO<sub>4</sub>Na surfactant formulation. The general trend of results showed significant detergency (>80% removal) at HLDs ranging between -3.0 and 0.0 and maximum soil removal (>90%) was achieved at the HLD = 0 for all oils studied. These results demonstrate that good detergency was found in widely varying salt concentration ranges (ranging from 0.6% to 23.8% NaCl) but collapsed to a similar HLD range (-3.0 to 0.0) for all soils studied. Granted, there are a few exceptions (e.g., EACN = 7.5 was > 80% removal at HLD = -4.0 to -5.0) but overall the -3.0 to 0.0 range appears best for the majority of the systems. More importantly, these results corroborate the hypothesis that an optimal HLD range exists for desirable detergency performance.

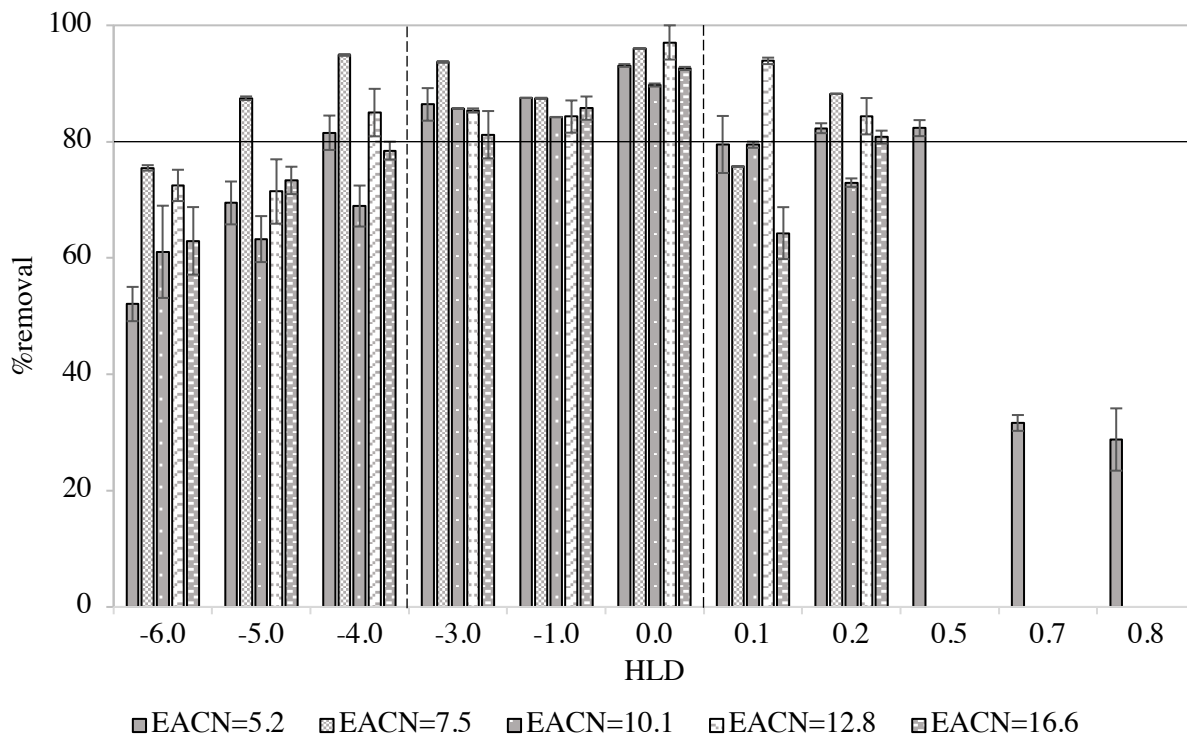


Figure 4.3 Correlation between detergency and HLD for all studied soils using 0.1 w/v% C<sub>10</sub>-4PO-SO<sub>4</sub>Na. Washing temperature was kept constant at 25 ± 1°C. The horizontal lines indicate a location of 80% removal. The vertical dash lines indicate an HLD region between -3.0 and 0.0.

***Correlation between detergency of selected soils with EACNs of 5.2 and 16.6, salinity and HLD using a binary surfactant mixture (C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio) as a confirmatory surfactant system***

To further corroborate the trends observed using C<sub>10</sub>-4PO-SO<sub>4</sub>Na alone, we next evaluated the detergency of the two soils with lowest and highest EACNs (EACNs = 5.2 and 16.6) at different NaCl concentrations using a binary mixture of C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio as a confirmatory surfactant system (Fig. 4.4a-b). The NaCl concentrations used in this work for the mixed surfactant system were calculated using the selected HLD range as shown in Fig. 4a-b and HLD parameters for the mixed surfactant system (K = 0.090 and C<sub>c</sub> = -0.80, data obtained from Fig. 4.1). The relationship between detergency, salinity, and HLD of the mixed surfactant system likewise showed that detergency increased with increasing salinities (negative HLDs), reached a

plateau at different salinity levels (HLDs approaching 0), and decreased with further increasing salinity levels beyond its  $S^*$  (HLDs  $> 0$ ). Once again, from Figure 4.4, it is observed that the best detergency ( $>80\%$  removal) occurred for HLD values ranging from -3.0 to 0.0, corroborating our initial results. In a comparison of optimum salinity ranges of the same oil for two different surfactant systems, the detergency performance of EACN values = 5.2 and 16.6 using the  $C_{10}$ -4PO- $SO_4Na$  and AOT surfactant mixture required lower salinity levels than those of  $C_{10}$ -4PO- $SO_4Na$  (Figs. 4.2a, 4.2e, 4.4a, and 4.4b). For instance, optimum salinity range for oil with EACN = 5.2 was in a range of 0.2– 21.4 w/v% NaCl for the  $C_{10}$ -4PO- $SO_4Na$  and 0.2 - 3.6 w/v% NaCl for the  $C_{10}$ -4PO- $SO_4Na$  and AOT mixture. This is consistent with previous discussion that the mixed surfactant system was more hydrophobic than the single surfactant due to less negative  $C_c$  value resulting in requiring lower amount of salt to drive the surfactant towards the oil-water interface and reach the optimum formulation (HLD = 0).

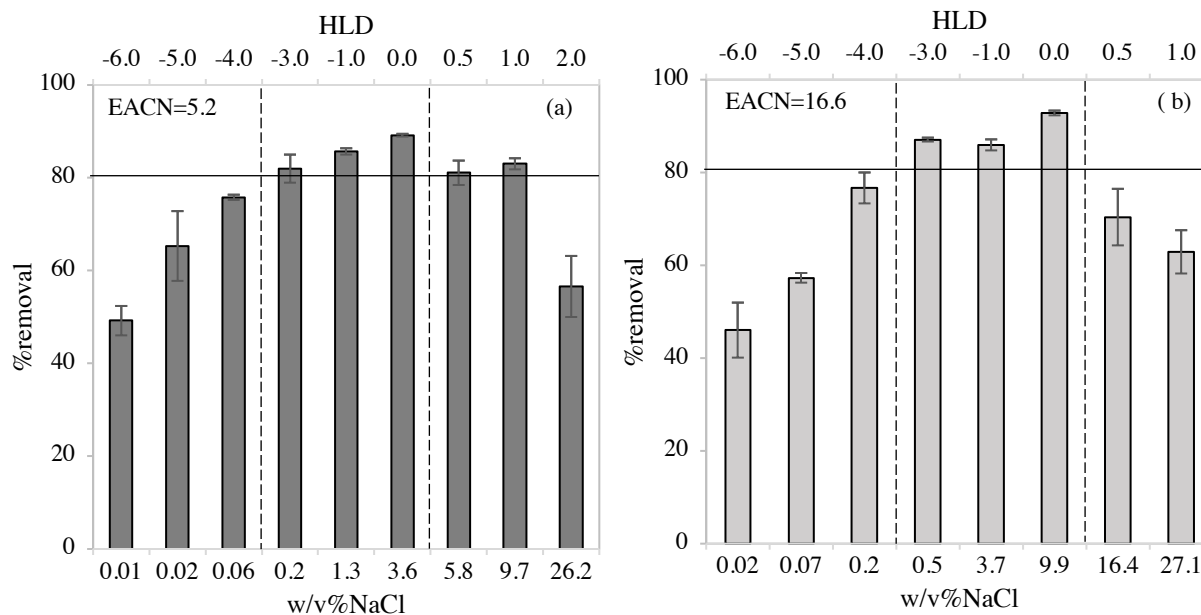


Figure 4.4 Detergency of soils with EACNs of **a)** 5.2 and **b)** 16.6 at various salinity levels and corresponding HLD values using a binary surfactant mixture of  $C_{10}$ -4PO- $SO_4Na$  and AOT at 1:1 by molar ratio. Washing temperature was kept constant at  $25 \pm 1^\circ C$ . The horizontal lines indicate a location of 80% removal. The vertical dash lines indicate an HLD region between -3.0 and 0.0.

***Correlation between detergency of solid octadecane (EACN = 18) and HLD using a binary surfactant mixture between C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio***

The HLD concept is thus seen to be a valuable tool for designing detergency performance of studied oily soils using two different anionic surfactant systems. As one final step, we employed the HLD concept with detergency of octadecane (EACN = 18, melting point = 26 - 29°C) which behaved as a solid non-particulate soil at a washing temperature of 25°C. From Figure 4.5, it can be observed that detergency of octadecane significantly increased at NaCl concentration of 0.6 w/v% (HLD = -3.0), reached a plateau at NaCl concentration range between 0.6 and 11.2 w/v% (HLDs = -3.0 to 0.0) with soil removal efficiency approximately 90%, and declined at salt levels beyond the S\* (HLDs > 0). It is important to note that while the removal mechanisms of oily and solid non-particulate soils have been shown to be different (Chanwattanakit et al., 2017; Phaodee et al., 2019; Thompson, 1994; Tongcumpou et al., 2003), these preliminary results indicate that the HLD range between -3.0 and 0.0 still held for octadecane removal. Future research should further explore the HLD-detergency behavior of solid non-particulate soils.

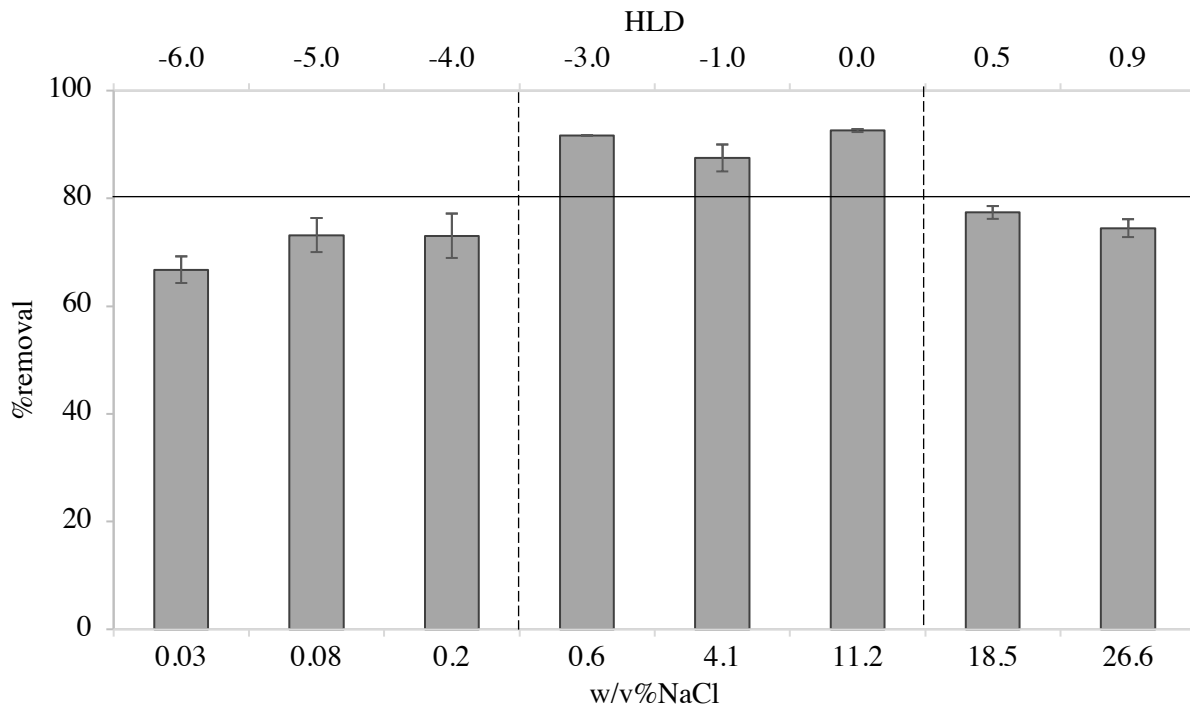


Figure 4.5 Correlation between detergency of octadecane (solid non-particulate soil), salinity and HLD using the binary surfactant mixture of C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio. Detergency experiment was done at 25 ± 1°C. Reported melting point temperature of octadecane is 26 - 29°C. The horizontal lines indicate 80% removal. The vertical dash lines indicate an HLD region between -3.0 and 0.0.

## Conclusions

Detergency of oily soils with EACNs varying from 5.2 to 16.6 and solid octadecane (EACN = 18) on polyester/cotton using different anionic surfactant systems was studied at a washing temperature of 25°C. Detergency exceeding 80% removal was accomplished at widely varying salinity values (0.6 – 23.8 w/v% NaCl for C<sub>10</sub>-4PO-SO<sub>4</sub>Na and 0.2 – 9.9 w/v% NaCl for mixed C<sub>10</sub>-4PO-SO<sub>4</sub>Na and AOT at 1:1 by molar ratio). Maximum detergency was demonstrated at optimum conditions (S\*) for all soils studied. When the results were interpreted using the HLD equation, good detergency was found to be in the same HLD range of -3 to 0 (Type I to optimum Type III microemulsions) for both liquid and solid nonparticulate soils with the maximum detergency at the HLD = 0. The significant improvement (>80% removal) in detergency of oily soils was found to correlate with IFT values less than 1 mNm<sup>-1</sup>. Further, detergency of solid octadecane likewise demonstrated that the HLD range of -3 to 0 showed superior detergency performance versus surfactant systems outside this HLD region. The current work thus supports the HLD method as a valuable tool for designing an optimum detergency formulation for widely varying EACN of oily and solid non-particulate soils.

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## Chapter 5 Conclusions

Although the effects of surfactant, temperature and removal mechanisms on detergency of oily soil have been extensively studied, additional research is required to examine the correlation between detergency and existing HLD concept. Currently, the study on detergency of solid-non particulate soil is still limited. The goals of this dissertation were to design and characterize detergency formulations of a wide range of soils while also providing a basis for a removal mechanism concept. This research was divided into 2 main topics. The first topic was to investigate surfactant systems capable of significantly improving detergency of triacylglycerol solid non-particulate soils below their melting point. This work studied the effects of surfactant, alcohol additives, and relevant removal mechanisms of the soil (Chapters 2 and 3). The second topic was to assess the utility of HLD concept as a design approach for detergency of varying types of soils (Chapter 4). In a move towards addressing the second research problem, this study examined detergency of widely varying EACN values and states of soils at different HLD values using two different surfactant systems.

In Chapter 2, a branched  $C_{14-15}$ -8PO-SO<sub>4</sub>Na surfactant was selected as a primary surfactant system to evaluate detergency of coconut oil below its melting point. Cold-water detergency of coconut oil at 10°C was found to be poor using the surfactant alone. With regards to salt concentration, this study found that detergency improved with increasing salt concentrations and reached maximum efficiency at  $S^*$  (Figure 2.1). This study found that the efficacy of detergency decreased while further increasing salt concentrations beyond the  $S^*$ . Improved detergency was observed with the addition of intermediate-chain alcohols (Figure 2.2). The  $S^*$  required in the surfactant system decreased from 8 w/v% NaCl for no alcohols to 4 w/v% NaCl for 1-octanol. Exceeding 90% removal reached with the addition of 90 mM 1-octanol (initial concentration) in a 0.1 w/v%  $C_{14-15}$ -8PO-SO<sub>4</sub>Na with added salt at 4 w/v% NaCl (the  $S^*$ ) system (Figure 2.5). Further studies showed that decreasing 1-octanol concentration from 90 mM (1.2 w/v%) to 15 mM (0.2 w/v%) still maintained detergency over 90% removal (Figure 2.6). Specifically, enhanced cold-water detergency of coconut oil was found to correlate with a reduction in IFT and improve wetting of the soil surface (Figure 2.2 and Table 2.2). However, melting point alteration of the soil, removed soil particle size, and dispersion stability did not appear to be an important factor in detergency

improvement (Tables 2.3 and 2.4). The use of intermediate-chain alcohols also provided robust results for other surfactant systems studied ( $C_{10-16}$ -7EO-OH and a mixture of  $C_{10-18}$ PO-2EO- $SO_4Na$ +SDOSS at 0.24/0.76 molar fraction with 0.5 w/v% NaCl), in addition another solid non-particulate soil (in this case, palm kernel oil) was examined (Figures 2.3 and 2.4).

In Chapter 3, this work further explored optimized surfactant systems capable of providing cold-water detergency comparable to that of systems presented in Chapter 2. The effects of anionic extended surfactant structure (e.g., linearity degree and number of EO groups), use of branched octanols as a presentative of intermediate-chain alcohols on the detergency performance of coconut oil, were studied. The presence of linearity and insertion of EO groups in the  $C_{14-15}$ -8PO- $SO_4Na$  base-surfactant molecule did not improve coconut oil removal (Figure 3.2). Thus, the branched  $C_{14-15}$ -8PO- $SO_4Na$  surfactant was continued, for use, in investigating the effect of branched alcohols (2-octanol and 2-ethyl-hexanol). Branched octanols further reduced  $S^*$  required from 4 w/v% NaCl (1-octanol) to 2 w/v% NaCl (2-octanol and 2-ethyl-hexanol) (Figure 3.3). Comparing linear octanol to branched octanols in the surfactant system with added salt at its  $S^*$ , detergency with the presence of 2-octanol was comparable to that of 1-octanol; whereas, detergency slightly decreased with the addition of 2-ethyl-hexanol (Figure 3.4). The concentration of 2-octanol was then evaluated as a final optimized surfactant system step. Decreasing 2-octanol concentration from 90 mM (1.2 w/v%) to 38.5 mM (0.5 w/v%) maintained detergency exceeding 90% removal (Figure 3.6). Improved cold-water detergency of coconut oil corresponded to a combination of lowering IFT and improving wetting (Figures 3.1 and 3.5). In addition, detergency of coconut oil was found to increase with increasing solubilization (Table 3.2).

In Chapter 4, this work assessed the correlation between detergency of a wide range of soils and optimal HLD values. A single anionic surfactant system ( $C_{10-4}$ PO- $SO_4Na$ ) was used as a primary surfactant to conduct detergency of five oily soils with widely varying EACNs from 5.2 to 16.6 at a washing temperature of 25°C. The detergency of all oily soils studied increased with rising NaCl concentrations and decreased with further elevating NaCl concentrations over the  $S^*$  (Figure 4.2). Exceeding 80% removal of all soils was observed across a wide range of salt concentrations, and maximum detergency was attained at its  $S^*$  (Figure 4.2). When the optimal NaCl concentrations were converted to HLD values, the surfactant systems corresponded to an identical HLD range between -3 and 0 (Figures 4.2 and 4.3). Improved detergency was found to correlate with a

reduction in IFT (less than  $1 \text{ mNm}^{-1}$ ) (Figure 4.2). Detergency of oily soils with lowest and highest EACNs of 5.2 and 16.6 was then evaluated using a binary surfactant mixture between  $\text{C}_{10}\text{-4PO-SO}_4\text{Na}$  and AOT at 1:1 by molar ratio as a confirmatory surfactant. Likewise, detergency over 80% was found at different NaCl concentrations corresponding to HLD values between -3 and 0 (Figure 4.4). Finally, detergency of a solid non-particulate (octadecane) was performed using the mixed surfactant systems, demonstrating that surfactant systems with HLD values between -3 and 0 showed the most effective detergency comparing to other HLD values (Figure 4.5). Thus, the results of this study support that the utilization of the HLD concept in detergency application is proven to be a potential tool to design optimum detergency formulations for a wide range of soils.

#### Recommendation for future research

The results of this research showed that cold-water detergency of solid non-particulate soils can be significantly improved with the addition of intermediate-chain alcohols in the surfactant formulations. Further research is required for mixed surfactant systems between anionic extended surfactant and nonionic surfactant to possibly reduce the use of alcohol in the detergency formulation. In addition, animal-based fat solid non-particulate soils (e.g., bacon grease, lard, and tallow) and cosmetic-based solid non-particulate soils (e.g. lipstick) require further investigation.

To further demonstrate HLD-detergency behavior, the HLD concept can be modelled by two different equations depending on the charge of surfactant head group. The use of single nonionic surfactant should be evaluated to determine an optimal HLD range and then move to more complicated surfactant system (e.g., a mixture between anionic and nonionic surfactant systems which will be close to the commercial detergent formulation). The current research did not evaluate varying soil-fabric types and their potential influence on the optimal HLD range. Therefore, the detergency effect on different types of fabric should be considered for future research.

## **Appendix A Evaluating the effect of crystal form of solid triacylglycerol on detergency**

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If the COVID-19 pandemic had not interrupted, this work would have been one of the chapters in this dissertation.

### **Introduction**

Fats are primarily composed of triacylglycerols or triglyceride (TAG). A TAG consists of three fatty acids bounded with triester of glycerol. The fatty acids are found in a wide variety of forms, which include short and long chain, saturated and unsaturated, odd or even carbon number, trans- or cis-, linear or branched combination (Small, 1986). Polymorphism is a unique characteristic of fat networks that affects their rheological characteristics. Polymorphism is the capability of solid fats to orient into several crystalline forms with identical chemical compositions in their liquid state (Widlak et al., 2001). Polymorphic forms are typically able to pack into three different crystal structures (alpha, beta prime, and beta) (Garti and Sato, 1988). The transition pathway of TAG is liquid to alpha, to beta prime and eventually to the optimum packing of the molecules which is beta form (Widlak et al., 2001). The alpha polymorph is most readily formed from the melt during the crystallizations at high cooling rates. The alpha is packed in a loose hexagonal subcell conformation which has a low density of the loose packing of the TAG molecules causing lowest crystal phase (Widlak et al., 2001). However, the alpha crystal remains small for a short period of time regarding its low stability and will eventually transform through the melt or molecular reorientation in the solid state to be the more stable beta prime phase (Ten Grotenhuis et al., 1999). The beta prime polymorph conformation can be obtained through the melt or alpha transition at intermediate cooling rates. The beta prime arranges in either a double- or triple-chain configuration and reorients in a more dense orthorhombic subcell structure of the beta polymorph (Breitschuh and Windhab, 1998). The beta form is the most stable form reflecting largest crystal in size, highest packing density, and highest melting point temperature. The beta structure can be formed directly

through the melt or beta prime transition under very slow heating rates. Practically, beta form is only obtained from solvents (Hernqvist, 1990).

These crystal forms can be distinguished by the difference in long spacing using X-ray diffraction (XRD) (Ahmadi et al., 2008; Garti and Sato, 1988). In addition, the differential scanning calorimetry (DSC) technique has been also used to characterize TAG mixtures and crystal phase formation regarding the difference in melting point of each polymorphic form (Himawan et al., 2007; Windbergs et al., 2009). DSC has been extensively utilized to understand TAG behavior and phase transition under different conditions in food industry (Garti et al., 1982; Maruyama et al., 2014). However, only limited research has shown that thermal analysis using DSC apparatus was a reliable technique to analyze crystal phase formation and also trace amount of residue after washing cycle in the detergency process. Yatagai et al., (1989) found a DSC endothermic peak decreased with increasing washing time indicating higher oily soil removal. After the contact of an aqueous surfactant (5% SDS solution), a broad endothermic peak appeared between the melting peaks of oily soils and frozen water suggesting a formation of ternary liquid crystal. Later, Yatagai et al., (1992) studied tripalmitin removal on fibrous and non-fibrous surfaces using a DSC technique. This work studied tripalmitin removal (obtained from solvent solution) which yielded beta tripalmitin crystal on the surface. The beta tripalmitin was conducted detergency at 20°C (solid non-particulate at the wash condition) and the results showed that the endothermic peak area declined with an increase in washing time and corresponded higher soil removal (Yatagai et al., 1992).

The current research is motivated by Scheuing's work which studied tristearin removal using Fourier transform infrared spectroscopy (FT-IR) (Scheuing, 1990). After the soil contacting with nonionic surfactant, alpha tristearin was readily removed and alpha to beta transition was also shown. However, beta tristearin was more resistant to removal indicating lower soil removal (Scheuing, 1990). Most of previous work on detergency of solid non-particulate soil were dissolved in solvents, which yielded beta crystal phase after the solvents evaporated off (Hernqvist, 1990). There has been limited work on quantitatively studying the effect of individual TAG polymorphic form on cleaning efficiency. Thus, this work attempts to investigate detergency of alpha and beta TAG and also evaluate the effect of substrate (DSC aluminum surface, cotton, 65/35

polyester/cotton blend, and polyester) on two forms of solid TAG removal. DSC is carried to analyze crystal formation and phase transition after detergency process.

## **Experimental Procedures**

### ***Materials***

Tristearin (>99%) and tetrahydrofuran were supplied by Sigma Aldrich. The anionic extended surfactant (C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na) with 93.84% active was received from Sasol North America, Inc. (Lake Charles, LA, USA). Bleached pure cotton, 65/35 polyester/cotton blend, and spun polyester Type 54 were purchased from Test Fabrics, Inc. (West Pittston, PA, USA). Aluminum DSC pans and covers were purchased from Perkin Elmer.

### ***Methodology***

#### *Thermal analysis*

Thermal analysis was performed to analyze the tristearin crystal formation and phase transition using a DSC Q100 (TA). Tristearin samples (approximately 1 mg) were weighted into DSC aluminum pan. The apparatus was heated from 40°C to 100°C with a heating rate of 70°Cmin<sup>-1</sup>. All experiments were conducted triplicate.

#### *Detergency experiments*

##### *Sample preparation on fabric procedure*

Five (5) w/v% tristearin solutions were prepared in tetrahydrofuran (THF). The oil solution (approximately 10 mL) was then dropped onto the fabric. After that, the soiled samples were left for 10 minutes to allow the THF to evaporate off which left the solid tristearin on the fabric.

##### *Alpha sample preparation on fabric*

The post-soiling samples were re-melted at 100°C for 10 minutes to allow the tristearin to completely melt, then the temperature was adjusted to 60°C for 5 minutes on an isothermal temperature hotplate, and cooled down under ambient condition. After the cooling down process, the samples were kept for another 10 minutes prior to detergency experiments.



### *Beta sample preparation on fabric*

The post-soiling samples were re-melted at 100°C for 10 minutes to allow the tristearin to completely melt. This step was carried out on an isothermal hotplate. The samples were then placed in an isothermal temperature oven at 60°C for 30 minutes. After 30 minutes, the samples were taken out of the oven and cooled down under ambient conditions. After cooling down, the samples were kept for another 10 minutes prior to detergency experiments.

### *Detergency Procedure*

For aluminum surfaces, and to avoid the samples hitting the spindle mixing stick and bouncing off, the DSC covers were adhered, using mounted glue, to the bottom of the washing bucket for the entire detergency experiments. However, the fibrous samples were freely submerged in the washing solution. Detergency was carried out at temperatures of  $25\pm 1^\circ\text{C}$  (below the melting points of alpha and beta samples) using a Terg-O-Tometer (Model 7243; USA Testing Co., Inc., Hoboken, NJ, USA). A 20-min wash cycle was performed for washing with 1 L surfactant solution. A 3-min first rinse and a 2-min second rinse were performed with 1 L DI-water. Washing and rinsing cycles were at a 120 rpm agitation speed. The bath temperature was kept constant during the washing and rinsing steps. After wash and rinse cycles, washed samples were laid down for aluminum surfaces, and hung to dry, using a clothespin, for 2 hours for fabrics. The detergency was determined by dividing the mass of removed soil, after wash, to the mass of initial oil soiled. All laundry experiments were repeated in triplicate and the error bars presented in the detergency results were standard deviations. Total detergency experiment duration (counting from sample preparation to drying step after wash) were completed within 4 hours to prevent phase transition

## **Results and Discussion**

### *Heating rate selection for evaluating tristearin crystal formation*

Approximately 1 mg tristearin was prepared on a DSC aluminum pan and then heated to 100°C, held at 67°C for 2 hours, and cooled to 25°C using cooling rate of 0.2°C/min to evaluate crystal formation. Heating rates were varied from 30°C/min (Fig. A-1a), 50°C/min (Fig. A-1b), and to 70°C/min (Fig. A-1c) to suppress the recrystallization of alpha to beta (peak appeared at around

67°C). The DSC thermograms showed that the recrystallization downward peak (exotherm) of alpha to beta (circled in Fig. A-1a and b) was prevented using a higher heating rate (70°C/min). Thus, a 70°C/min heating rate was selected to determine the individual amount of alpha and beta present in the samples (the maximum capacity of the DSC apparatus used is 100°C/min). This heating rate is reasonably high for DSC, but previous work has proven that the use of high heating rate is reliable (Danley et al., 2008; Goth et al., 2003; Gramaglia et al., 2005; Pijpers et al., 2002).

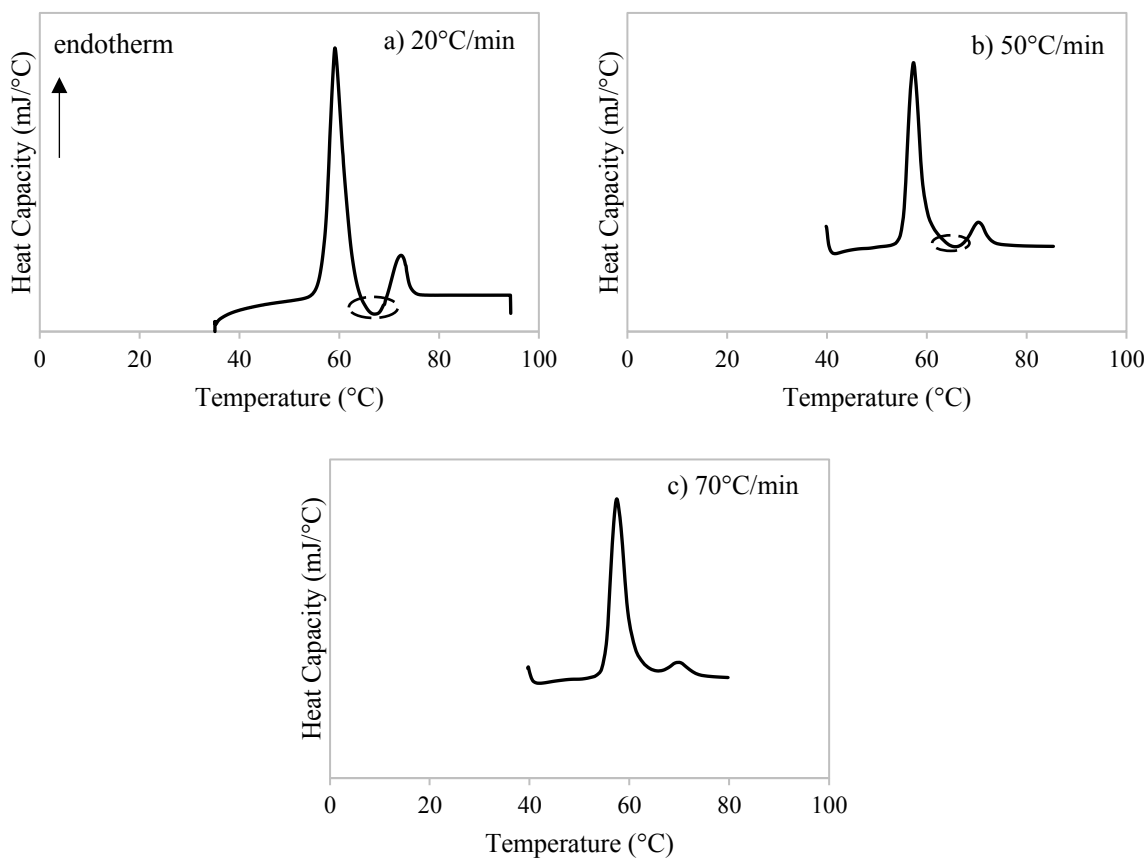


Figure A-1 Effect of heating rate on DSC thermogram of tristearin. About 1 mg tristearin was heated to 100°C, held at 67°C for 2 hours, and cooled to 25°C using cooling rate of 0.2°C/min. The samples were then heated to 80°C using heating rates of **a)** 30°C/min **b)** 50°C/min **c)** 70°C/min, respectively. Upward peak indicates endotherm and downward peak indicates exotherm.

## Crystal formation Results

### Pure alpha formation

About 1 mg solid tristearin was added on a DSC aluminum pan, heated to 100°C for 10 minutes, and cooled to 60°C for 5 minutes. These steps were all conducted using a hotplate. Then the sample was cooled under ambient temperature and aged for additional studied times: no aging, 12 hours, and 24 hours (Fig. A-2), respectively. This experimental procedure resulted in a formation of pure alpha with the melting point about 55°C (Windbergs et al., 2009) as shown in Fig. A-2. Comparing the aging time, a transition of alpha to beta was observed after aging for 24 hours under an ambient condition. Thus, this preparation method would be carried out to prepare the alpha on fabrics and detergency of alpha would be completed within 12 hours to further the transition of alpha to beta.

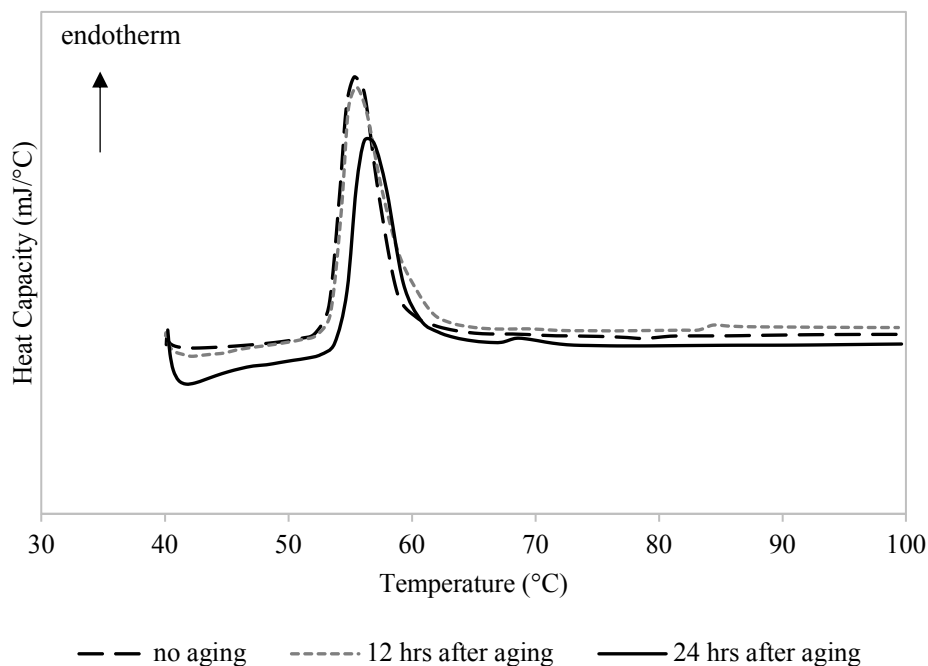


Figure A-2 Effect of aging time on alpha to beta tristearin transition using heating rate of 70°C/min

### Pure beta formation

About 1 mg solid tristearin was put on an aluminum DSC pan, heated to 100°C for 10 minutes using a hotplate and cooled to 60°C for 30 minutes in an isothermal incubator. Then the sample

was cooled under an ambient temperature and aged for an additional period of time: no aging and 24 hours (Fig. A-3). This experimental procedure showed a formation of pure beta form with melting point of 73.7°C (Windbergs et al., 2009) and revealed that the beta form is time independent within 24 hours (Fig. A-3) due to the most stable form.

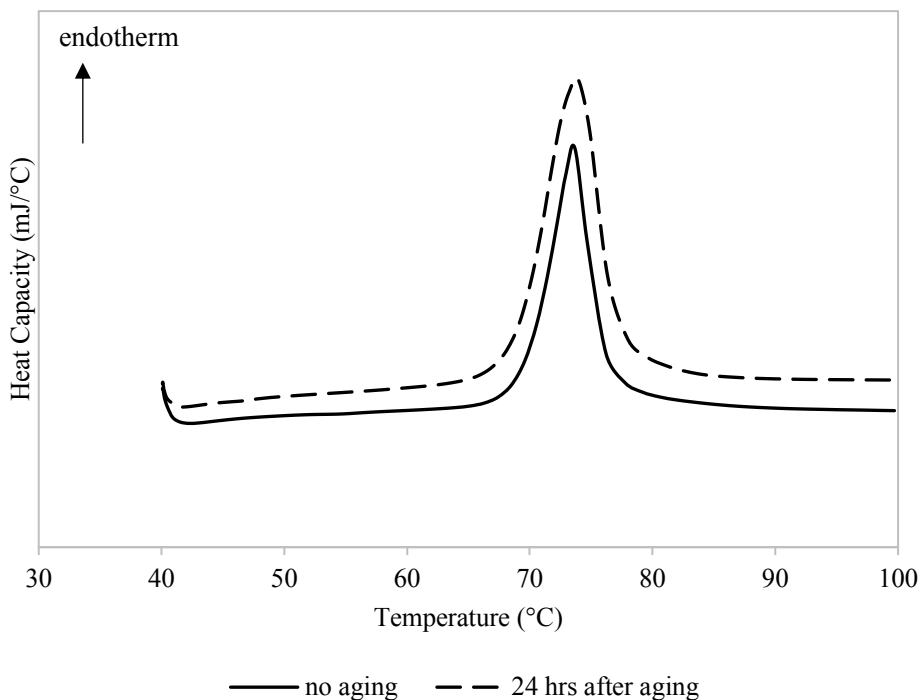


Figure A-3 Effect of aging time on beta tristearin formation using heating rate of 70°C/min

#### ***Preliminary detergency results on aluminum surface***

The alpha and beta samples were next utilized in preliminary detergency studies to determine the effect of crystal form on removal efficiency in 0.1 w/v% C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na. The results show that neither the alpha nor beta samples was removed from the aluminum surface in a wash solution with varying washing times up to 40 minutes. However, the post-wash alpha samples were further analyzed in a crystalline phase transition using DSC heating cycle as shown in Fig. A-4. The results showed that there was a slight transition of alpha to another phase at 69.2°C with the presence of the surfactant. Scheuing (1990) also observed a phase transition of alpha to beta with the exposure of nonionic surfactant using FT-IR.

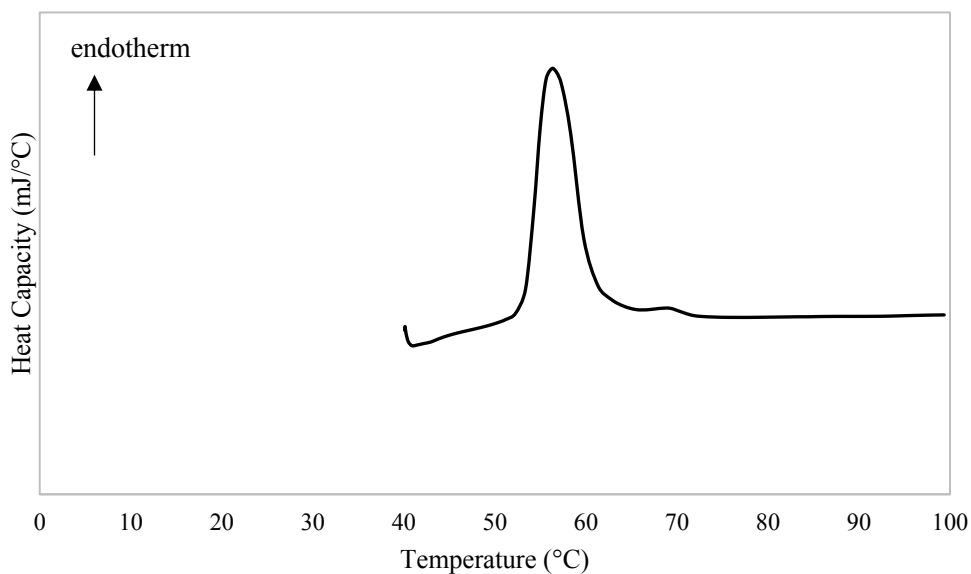


Figure A-4 DSC thermogram of post-wash alpha sample. Detergency was carried out for 20 minutes at 20°C. Heating rate was 70°C/min.

### Next Steps

If the COVID-19 pandemic had not interrupted my research, the next steps would have been

- 1) performing detergency of alpha and beta tristearin on cotton, 65/35 polyester/cotton, and polyester
- 2) measuring contact angle through a surfactant droplet on each substrate using sessile drop analysis

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## Appendix B Effect of surfactant concentration on detergency of different coconut oil states

Surfactant formulation : branched C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with added salt at S\* (8 w/v% NaCl)

The IFT measurement results showed critical micelle concentration (CMC) and critical microemulsion concentration (C<sub>μ</sub>C) of C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with 8 w/v% NaCl were 0.007 w/v% (700 ppm) and 0.6 w/v% (6000 ppm) as shown in Fig. B-1.

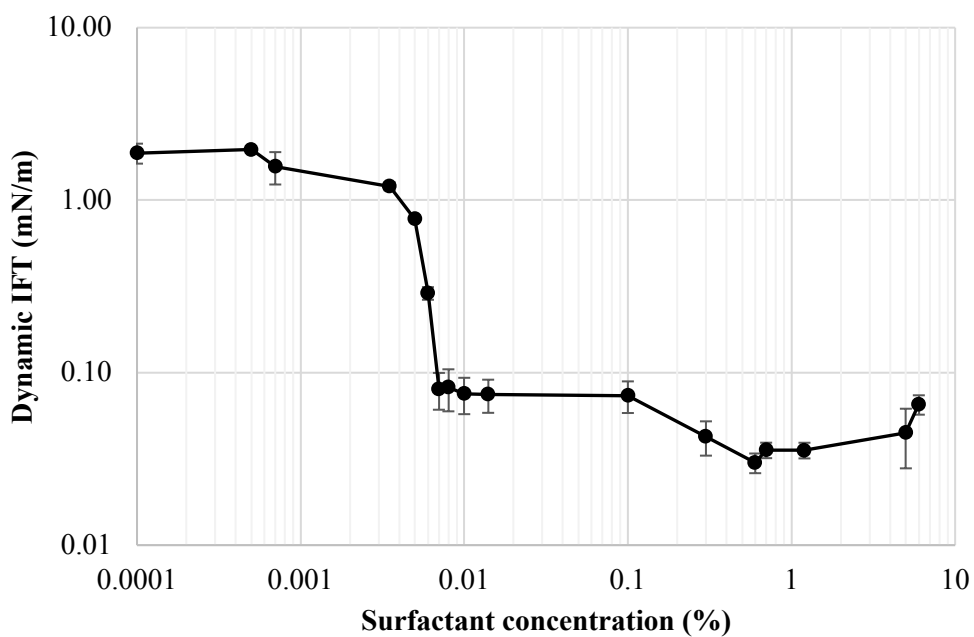


Figure B-1 IFT measurements using C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with 8 w/v% NaCl at 30°C



Surface tension measurements were carried out using a Wilhelmy plate method to determine CMC between aqueous and air at 30°C. The interception of the linear lines was a value of CMC which found to be 0.0015 w/v% (Fig. B-2).

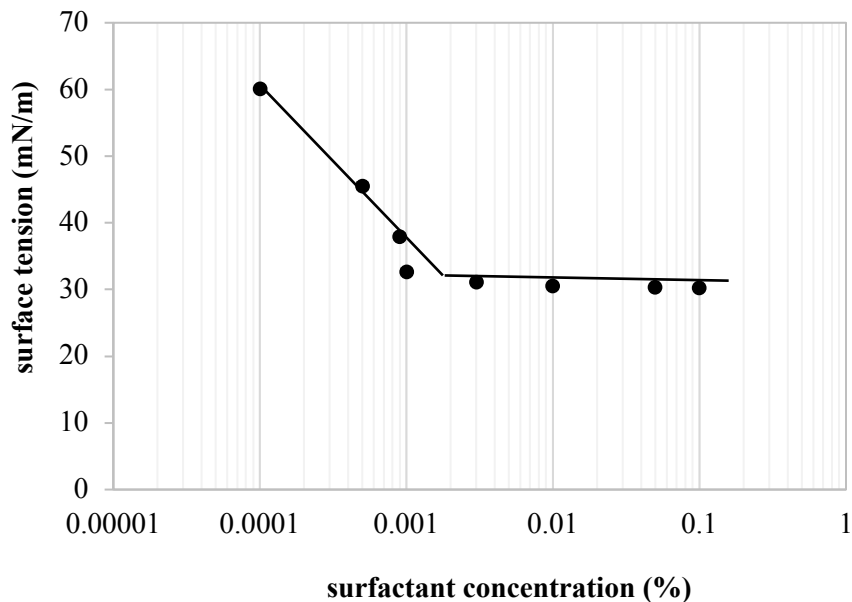


Figure B-2 Surface tension measurements at 30°C. Surfactant system studied was C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na with 8 w/v% NaCl

Figure B-3 shows detergency of semisolid coconut oil at 10°C, liquid coconut oil at 30°C, and IFT measurements at different surfactant concentrations with added NaCl at 8 w/v%. Generally, detergency of semisolid coconut oil was poorer than that of liquid coconut oil using all studied surfactant systems. The optimal detergency of liquid coconut oil (~80% removal) was observed at CMC obtained through IFT measurements. However, higher surfactant concentration (0.1 w/v% C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na) was required to attain optimal detergency of semisolid coconut oil.

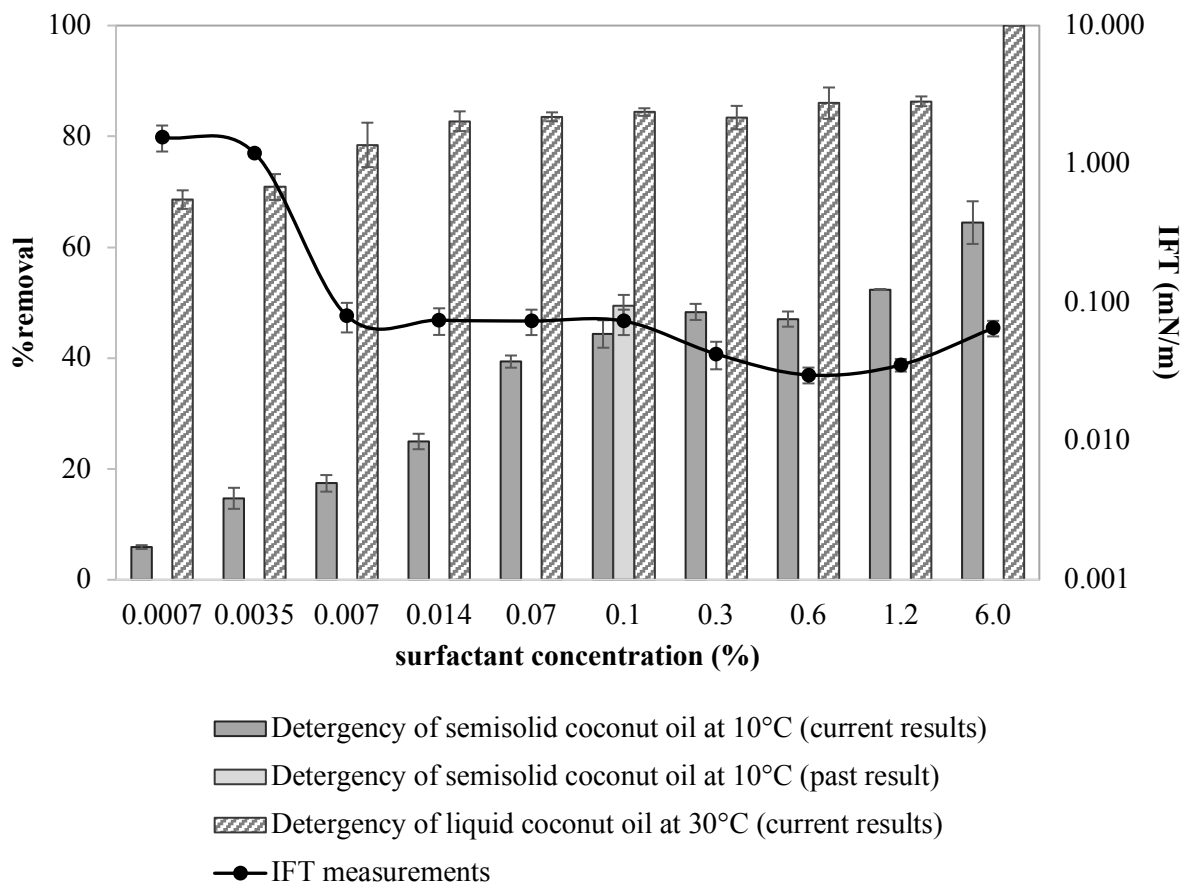


Figure B-3 Correlation between detergency of liquid and semisolid coconut oil and IFT at different surfactant concentrations. Surfactant concentrations of C<sub>14-15</sub>-8PO-SO<sub>4</sub>Na was varied with the addition of salt at 8 w/v% NaCl.