MECHANISM AND PERFORMANCE
OF SOLID NON-PARTICULATE SOIL
(WAXY SOLID) REMOVAL FROM FABRICS

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ABSTRACT

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Keywords: Solid non-particulate soil/ Solid fat soil/ Methyl palmitate/ Extended surfactant/ Laundry detergency

Methyl palmitate or palmictic acid methyl ester was used as both a model solid fat and an oily soil was removed from cotton and polyester above and below the melting point. Surfactants studied were extended surfactants ($C_{12,13}$-4PO-SO_4Na , $C_{12,14}$-10PO-2EO-SO_4Na and $C_{12,14}$-16PO-2EO-SO_4Na), alcohol ethoxylate (EO9), sodium dodecyl sulfate (SDS), methyl ester sulfonate (MES), methyl ester ethoxylate (MEE), and mixed surfactants between extended surfactant ($C_{12,13}$-4PO-SO_4Na) and sodium mono- and dimethyl naphthalene sulfonate (SMDNS). Above the melting point (~30 ºC) of methyl palmitate, the maximum oily soil removal was found to correlate well with the lowest dynamic interfacial tension (IFT) with increasing washing temperature and salinity. Therefore, roll-up of liquid soil is an important mechanism. Below the melting point, the detergency efficiency was high corresponding to the low contact angles (indicating high wettability) of the wash solution on the methyl palmitate surface for all studied surfactants. The solidified methyl palmitate was dislodged from fabric surface and dispersed in the wash solution as small solid particles by surfactant penetration resulting from wetting the surface rather than solubilization. Therefore, surfactant and salinity improves wetting, dispersion stability, and decreases detached particle size. Unlike particulate soil, electrostatics is not the primary driving force for solid non-particulate soil detergency.

บทคัดย่อ

จรัสศรี ชาญวัฒนกิจ : กลไกและประสิทธิภาพการกำจัดคราบน้ำมันกึ่งแข็งกึ่งเหลวออกจากผิวผ้า (Mechanism and Performance of Solid Non-Particulate Soil (Waxy Solid) Removal from Fabrics) อ. ที่ปรึกษา : ศ.ดร. สุเมธ ชวเดช, ศ.ดร. จอห์น เอฟ สกามีฮอร์น, และศ.ดร. เดวิด เอ สปาทินี่ 162 หน้า

งานวิจัยนี้ใช้เมทิวปาร์มมิเทตหรือปาร์มิติกเมทิลเอสเทอร์เป็นต้นแบบคราบน้ำมันกึ่งแข็งกึ่งเหลวที่ต้องการแยกออกจากผ้าคอตตอนและผ้าโพลีเอสเตอร์ที่อุณหภูมิเหนือและต่ำกว่าจุดหลอมเหลวของน้ำมันเมทิวปาร์มมิเทต สารลดแรงตึงผิวที่ใช้ในงานวิจัยนี้คือ $C_{12,13}$-4PO-SO_4Na , $C_{12,14}$-10PO-2EO-SO_4Na and $C_{12,14}$-16PO-2EO-SO_4Na, alcohol ethoxylate (EO9), sodium dodecyl sulfate (SDS), methyl ester sulfonate (MES), methyl ester ethoxylate (MEE), และสารลดแรงตึงผิวผสมระหว่าง $C_{12,13}$-4PO-SO_4Na และ SMDNS เหนือจุดหลอมเหลวของเมทิลปาร์มิเทต ประสิทธิภาพการกำจัดคราบน้ำมันได้สูงซึ่งพบว่าสัมพันธ์กับค่าแรงตึงผิวน้อยที่สุดเมื่อเพิ่มอุณหภูมิน้ำซักและการใช้เกลือ ดังนั้นการกำจัดคราบน้ำมันชนิดเหลวด้วยวิธีโรลอัพเป็นกลไกที่สำคัญต่ำกว่าจุดหลอมเหลวของเมทิลปาร์มิเทต ประสิทธิภาพการซักจะมากเนื่องจากมุมสัมผัสระหว่างพื้นผิวน้ำมันแข็งกับสารลดแรงตึงผิวมีค่าน้อยที่สุด (ภาวะการเปียกของพื้นผิวมาก) ทำให้การกำจัดคราบน้ำมันมีประสิทธิภาพดีมาก น้ำมันเมทิลปาร์มิเทตที่ถูกทำให้แข็งจะถูกขจัดออกมาจากผิวผ้าและมีขนาดเล็กแขวนลอยอยู่ในน้ำซัก เนื่องสารลดแรงตึงผิวสามารถแทรกซึมเข้าไปในผิวน้ำมันเมทิลปาร์มิเทตที่ถูกทำให้แข็งด้วยการทำให้เปียกบนผิวน้ำมันเมทิลปาร์มิเทตก่อน ทั้งนี้กลไกการกำจัดน้ำมันวิธีดังกล่าวที่อุณหภูมิต่ำจะดีกว่ากลไกการละลาย ดังนั้นสารลดแรงตึงผิวและเกลือจะช่วยในการทำให้พื้นผิวน้ำมันเปียกเพิ่มความสามารถในการกระจายตัวของอนุภาคน้ำมัน และลดขนาดของอนุภาคน้ำมันหลังจากการหลุดออก ซึ่งจะไม่เหมือนกับการกำจัดคราบชนิดอนุภาคของแข็ง ที่แรงประจุไฟฟ้าไม่ใช่กลไกที่สำคัญสำหรับการกำจัดออกของน้ำมันชนิดนี้

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ABBREVIATIONS

IFT	Interfacial Tensoin
$C_{12,13}$-4PO-SO_4Na	Branched alcohol propoxylate sulfate sodium salt with 12-13 carbon number with approximately four propylene oxide (PO) units
$C_{12,14}$-10PO-2EO-SO_4Na	Sodium linear-alkyl polypropoxylated polyethoxylated sulfate with 12-14 carbon number with approximately 10 propylene oxide (PO) and two ethylene oxide (EO) units
$C_{12,14}$-16PO-2EO-SO_4Na	Sodium linear-alkyl polypropoxylated polyethoxylated sulfate with 12-14 carbon number with approximately 16 propylene oxide (PO) and two ethylene oxide (EO) units
EO9	Alcohol ethoxylates with a C12 to C14 alkyl chain length and 9 ethylene oxide
SDS	Sodium dodecyl sulfate with a C12 alkyl chain length
MES	Methyl ester sulfonate with a C14 alkyl chain length
MEE	Methyl ester ethoxylate with a C12 alkyl chain length and 18 ethylene oxide
SMDNS	Sodium mono- and dimethyl naphthalene sulfonate
CMC	Critical micelle concentration
CμC	Critical microemulsion concentration
CD	Commercial detergent
PZC	Point of zero charge

CHAPTER I
INTRODUCTION

Textile cleaning is a complex process which has been investigated for decades (Chi *et al*., 1999; Tongcumpou *et al*., 2003 and 2005; Phan *et al*., 2009 and 2010). Laundry detergency can be defined as a process for removed of unwanted substances (soils) from fabrics by using the interaction between surfactant, soil, and substrate. Several factors can affect the efficiency of detergency such as the properties of surfactant (Linfield *et al.,* 1962), nature of solid surface (Christ *et al*., 1994), mechanical action during washing (Obendorf *et al*., 1982), water hardness (Tanthakit *et al.,* 2009), temperature and electrolyte level (Tanthakit *et* al., 2011) and other additives (builder, enzymes, and anti-redeposition agents) (Webb *et al*., 1988). All studies of oily soil detergency used liquid oil as a model of soil in detergency. Our previous research works focusing on oily soil detergency using different liquid oils have found good correlation between detergency efficiency and ultralow interfacial tension (IFT), generated by Winsor type III microemulsion formation (Tongcumpou *et al*., 2003 and 2005; Tanthakit *et al.,* 2008, 2009, and 2013) . Recently, our research group has published studies of the mechanisms of particulate soil detergency using carbon black as a model hydrophobic soil and kaolinite and ferric oxide as model hydrophilic soils. The detergency performance was correlated to surfactant type and concentration, pH, and fabric type by using the basic parameters of spreading pressure and surface adsorption at the interface between soil/solution, zeta potential, and wettability (Rojvoranun *et al*., 2012).

Solid non-particulate soil is a special type of oily soil which exhibit properties between liquid and solid, depending on temperature. This type of soil becomes an essential problem in laundry detergency process which can be considered to represent as a waxy solid staining on clothes. This special type of soils becomes a challenging problem in laundry detergency, especially in a cold climate region under a low temperature. These stained oils are mixtures between liquid and solid oils in which the liquid oil is entrapped in the crystal structure of solid oil under a moderate temperature, causing it to be hard to remove. According to the literature, few studies were reported on cold-water detergency of solid non-particulate soil or solid fat soil because important variables such as soil/bath interfacial tension (IFT) and surfactant adsorption onto the surface of solid fat soil cannot be measured (Chaudhuri and Paria, 2009). Scheuing (1990) studied the detergency mechanism of tristearin (model solid fat soil) by using Fourier transform infrared spectroscopy (FT-IR) and reported that the removal of solid triglycerides from surface was more complex than solid hydrocarbon soils because of the polymorphism in the crystal structure of tristearin. Morris and Prato (1982) found that the best removal of particulate and oily soil from cotton fabric was at high temperature, whereas the nonpolar fraction of oily soil removed from polyester was better using a low wash temperature. Illman *et al.* (1970) found better removal of nonpolar sebum from Dacron or nylon in cold water than hot water. Kawase *et al.* (1991 and 1994) studied the removal mechanism of solid fatty acid soil by using nonionic and anionic surfactants reported that solubilization was the dominant mechanism to remove solid organic soil at low temperature. Therefore, studies on the removal mechanisms of solid non-particulate soil or solid fat soil below and above its melting point can lead to a better understanding and more effective formulation for solid non-particulate soil detergency.

In this research, methyl palmitate or palmitic acid methyl ester, a monoglyceride, having a melting point around 30 °C was used as a model solid fat or oily soil being removed from either hydrophilic surface (cotton fabric) or hydrophobic surface (polyester fabric) by using a single anionic extended surfactant for the first work (Chapter IV) and alcohol ethoxylate (EO9), sodium dodecyl sulfate (SDS), methyl ester sulfonate (MES), methyl ester ethoxylate (MEE), and two extended surfactants ($C_{12,14}$-10PO-2EO-SO_4Na and $C_{12,14}$-16PO-2EO-SO_4Na) for the second work (Chapter V) at different temperatures both higher and lower than its melting point. For detergency performance experiments above the melting point, IFT was measured in order to confirm the correlation between the IFT value and the percentage of oil removal whereas, for washing experiments below the melting point, several important factors such as zeta potential of oil particles and fabrics, contact angle, oil dispersion stability, particle sizes of detached methyl palmitate, and oil solubilization after the wash step were also measured and used to explain the mechanism of solid non-particulate soil detergency. In addition, the scanning electron microscopy (SEM) was also used to study the surface morphology of the studied fabrics before and after soiling with methyl palmitate and after washing under different studied conditions in order to clarify the oil detachment and re-deposition on both studied fabrics. For Chapter VI, mechanism and performance of methyl palmitate detergency under microemulsion-based formulation was investigated. Furthermore, the overall conclusions and recommendations are given in Chapter VII.

CHAPTER II
LITERATURE REVIEWS

2.1 Surfactants

Detergent products used in household laundry and commercial applications are complex formulations consisting of various types of chemical ingredients, which can be classified into three major groups; surfactants, builders, and auxiliary agents (Lange, 1994). Each component of the detergent products has its own specific function in cleaning process, but surfactants are the most important component in all types of detergent products (Jakobi and Löhr, 1987).

A surfactant or "surface active agent" is a substance that reduces significantly the surface tension of a liquid after the addition of surfactant. According to the lowering interfacial tension between two interfaces (e.g. water/soil, and soil/fabric), this helps increase ability to remove an unwanted substance from the solid surface such as textiles, clothes, and human skin. Surfactant structure generally contains a hydrophilic head (water-loving) that attracts to water molecules and a hydrophobic tail (water-hating) that repels water together with attaching itself to oil molecules, as shown in Figure 2.1. In addition, surfactant can improve the wetting ability of water, emulsification, and solubilzation and dispersion during washing process (Bajpai and Tyagi, 2007).

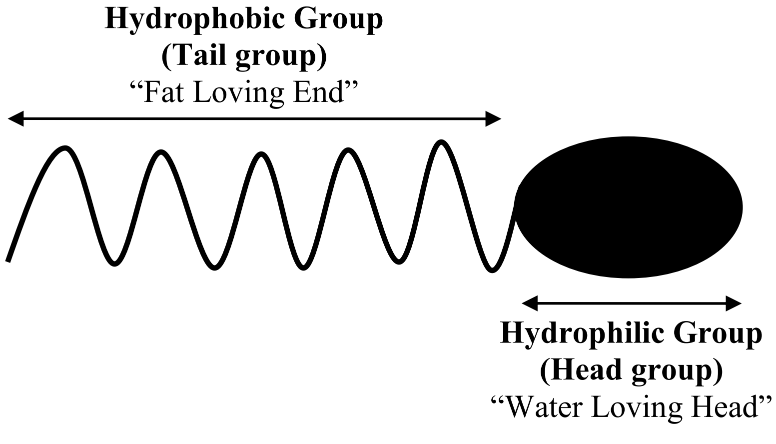


Figure 2.1 surfactant structures.

In general, the hydrophobic part can be a straight or branched long-chain hydrocarbon (or partially containing aromatic). In contrast, the hydrophilic part carries positive (cationic surfactant) or negative charge (anionic surfactant). Apart from ionic surfactants, the hydrophilic part (head group) of nonionic surfactant contains ethylene oxide, sugar, or saccharine group (Goddard and Ananth, 1993). Surfactant can be basically categorized in to 4 types, using the criterion of the charge type present in the chain-carrying portion of the molecule after dissociation in aqueous solution.

2.1.1. Anionic Surfactant

The hydrophilic head group has a negative charge, for example, $RCOO^- Na^+$ (soap), and $RC_6H_4SO_3^-Na^+$ (Alkyl Benzene Sulfonate).

2.1.2. Cationic Surfactant

The hydrophilic head group has a positive charge, for example, $RNH_3^+Cl^-$ (salt of a long-chain amine), and $RN(CH_3)_3^+Cl^-$(quaternary ammonium chloride).

2.1.3. Nonionic Surfactant

There is no charge present in the hydrophilic head group, so it can be more resistant to water hardness deactivation; for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long chain fatty acid) and $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenatedalkylphenol).

2.1.4. Amphoteric/Zwitterionic Surfactant

Both positive and negative charges are present in the hydrophilic portion; for example, $RN^+H_2CH_2COO^-$ (long chain amino acid) and $RN^+(CH_3)_2CH_2CH_2SO_3$ (sulfobetaine). The charge of this surfactant type also depends on pH of solution. At a low the pH (acidic solution), it has positive charge, and at a high pH (alkaline solutions), it has negative charge.

2.2 Extended Surfactant

An extended surfactant has a group of intermediate polarity, such as polypropylene oxide (POs) or polypropylene-polyethylene oxide (POs-EOs) group, inserted between the hydrophilic head and hydrocarbon tail group, as shown in Figure 2.2.

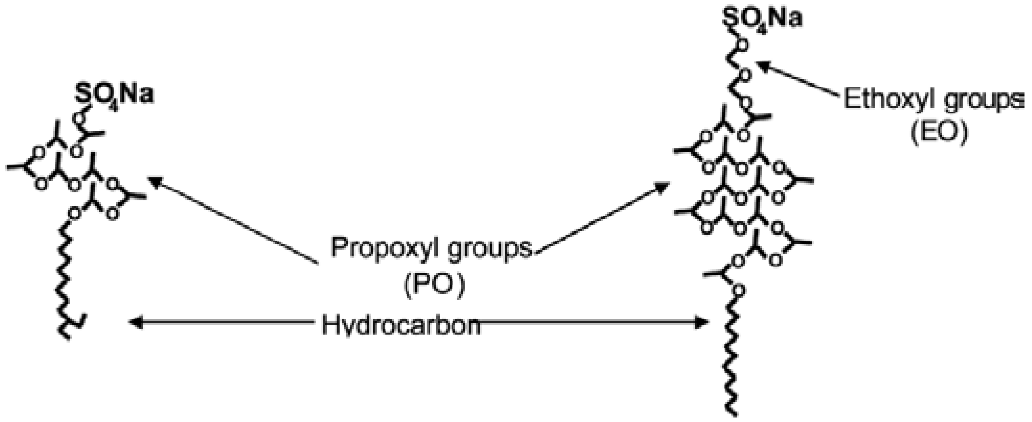


Figure 2.2 The structure of extended surfactant (Witthayapanyanon *et al*., 2008).

As the consequences of this unique structure, it can further stretch out into oil and aqueous phase, resulting in a smoother transition between the hydrophilic and hydrophobic regions at the interface. The presence of polypropylene oxide group in the hydrocarbon tail of surfactant molecule which provides more hydrophobic portion also helps extend the tail to the oil phase, while maintaining good interaction into the water phase. Hence, it is easy to form a middle-phase microemulsion, in which provides both high solubilization, and ultralow interfacial tension (IFT), leading to various applications such as extraction, separation,and cleaning (Witthayapanyanon *et al*., 2006 and Phan *et al*., 2011).

Miñana-Perez *et al.,* (1995) studied the solubilization of polar oils with extended surfactants. Alkyl polypropylene oxide ether sulfates (extended surfactant), were found to exhibit intermediate behaviors between anionic and nonionic surfactants. They showed three phases of microemulsions of a variety of long chain oils, especially for mono- and triglyceride esters using optimal formulation.

Witthayapanyanon *et al.*, (2006) studied the variations in dilute concentration of oil system and in different types of extended surfactant on the surfactant formulations. Sodium alkyl polypropylene oxide sulfate [$R\text{-}(PO)_x\text{-}SO_4Na$] and sodium alkyl polypropylene-polyethylene oxide sulfate [$R\text{-}(PO)_y\text{-}(EO)_z\text{-}SO_4Na$]were selected in the studies. The IFT values were measured as a function of electrolyte and surfactant concentration for polar and non-polar oils. The results showed that these extended surfactant systems had low critical micelle concentrations (CMC) and critical microemulsion concentrations (cμc) compared with the conventional surfactants. Besides, the ultralow IFT in different oils was achieved at ppm levels of these extended surfactant systems.

Velásquez *et al.*, (2009) studied the effect of temperature and other variables on the optimum formulation of anionic extended surfactant-alkane-brine systems, they found that the CMC and cloud point decreased with increasing number of propylene oxide groups (PON),indicating that the lipophilicity of the extended surfactant increased as PON increases. Moreover, the surfactant hydrophilicity was found to decrease with increasing temperature, which did not relate to the expected behavior of anionic species, probably due to the partial hydration of the initially first propylene oxide unit which are located close to the anionic head group.

Phan *et al.,* (2011) investigated the effects of extended surfactant structure on microemulsion formation and IFT values with different triglyceride oil. The results showed that at least 8 propylene oxide groups were required to obtain ultralow interfacial tension and a middle phase microemulsion with triglyceride oil. Furthermore, the extended surfactants with hydrocarbon branching structure seem to facilitate the ultralow interfacial tension.

2.3 Soils

Soils can be defined as contaminants on substrate, which can be divided into three categories; oily and greasy soils, particulate soils or solid soils, and stains.

2.3.1 Oily and Greasy Soils

Oily soils mean soil only composing of non-polar hydrocarbons such as diesel and motor oils, usually liquid and highly hydrophobic, which means that they do not mix well with water. Greasy soils mainly refer to triglycerides and their derivatives: mono- and triglycerides, and fatty acid. Molecular weight fatty acids are more polar but not polar enough to be dissolved by water.

2.3.2 Particulate Soils or Solid Soils

Examples of particulate soils are dust, clay, and metal oxides. There are several properties affecting the detergency performance such as size, shape, and surface geometry of soil. For instance, they are soluble neither in water nor in inorganic solvents, and they usually exhibit a large surface area, where oils and greases adsorb strongly. Particulate soils contribute significantly to the difficulty in removing oily and greasy soils due to their rigidification and catalyzing in an oxidation or cross-linking of unsaturated triglycerides. Since they are not water soluble, these particulate soils can be redeposited on the cleaned surfaces. It is important to keep these soils effectively dispersing on the washing liquid (Lance, 1994).

2.3.3 Stains

Coffee, tea, blood, ink, and fruit juices stains are the examples of stains. They can form physical or chemical bond with the substrate and result in difficult soil removal. Therefore, the substrate can be permanently stained by this type of soil.

2.4 Solid Non-Particulate Soils

Solid non-particulate soil or solid fat soil (waxy solid) is a special type of soil which has properties between liquid and solid, depending on temperature; for example, stiff dough, firm gelatin, butter, margarine, or solidified hamburger or bacon grease etc. Butter and margarine have a melting point between 30 to 35 °C. If it is heated above the melting point, it will gradually melt into liquid form. In contrast, if its temperature is below the melting point, it will be solid instead.

In this research, methyl palmitate or palmitic acid methyl ester (Figure 2.3) —one kind of solid oily soil— is selected to investigate the formation of middle-phase microemulsions with extended surfactants at various temperatures and to correlate the detergency performance of oil removal to microemulsion type at high temperatures greater than its melting point. Normally, methyl palmitate or palmitic acid methyl ester is a colorless liquid or crystalline with a boiling point of 185 °C and a melting point in the range of 29 to 32 °C. It can be soluble in both alcohol and ether solvents, and it is widely used in the fields of detergent, resin, plasticizer, lubricant, and animal feed. The information and properties of methyl palmitate are shown in the Table 2.1.

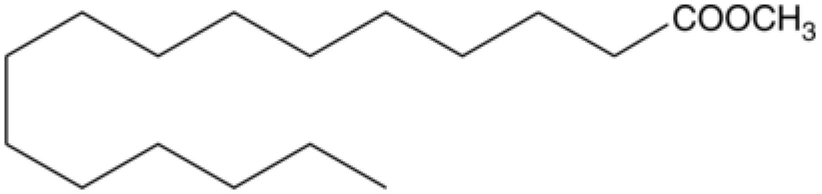


Figure 2.3 The molecular structure of methyl palmitate (Cayman, 2017).

Table 2.1 The information and properties of methyl palmitate (Cayman, 2017 and Sigma-Aldrich, 2017)

Properties	**Information**
Synonyms	Methyl hexadecanoate, Palmitic acid methyl ester
CAS number	112-39-0
Linear formula	$CH_3(CH_2)_{14}CO_2CH_3$
Molecular weight	270.45
Refractive index	*n*20/D 1.4512
Boiling point	185 °C/10 mmHg
Melting point	29–32 °C
Density	0.852 g/mL at 25 °C
Allergen	no known allergens
Flash point	113 °C

2.5 Contact Angle and Wetting

Contact angle is the physical parameter to indicate how well the solution wets the surface so it is a widely used method to characterize the surface wettability. A number of industrial processes such as printing, painting, adhesion, lubrication, coating, and cleaning essentially involve the phenomenon of wetting (Kumar *et al.*, 2007, Prabhu *et al.*, 2009, and Yuan *et al.*, 2013). Wetting of fabric and soil is an important for the soil removal so it is a related phenomenon but detergency is a complex mechanism involving with many variables. Therefore, the relationship between wetting and detergency is not simple (Kissa, 1981). Contact angle is a measure of the degree of wetting or wettability of a surface by a liquid. A drop of a liquid put on a solid will modify its shape until the equilibrium is attained. The balance of interfacial energies under equilibrium gives in equation 2.1. An angle of 180 indicates zero adhesion between the liquid and surface and therefore represents a total non-wetting condition and finally of course it has a perfectly non-wetted surface. For some liquids a zero contact angle is obtained and might also be called perfect wetting and hence spontaneous spreading. Another possibility is partial wetting, where a contact angle is subtended somewhere between 0° and 90°. An angle subtended between 90° and 180° in the liquid would be a non-wetting condition. These behaviors are shown schematically in Figure 2.4.

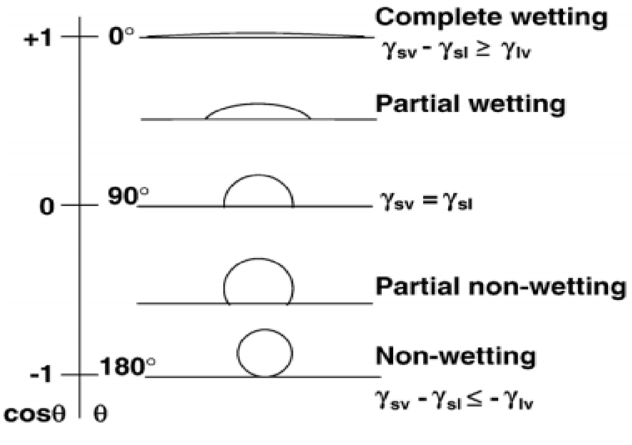


Figure 2.4 Liquid drop on a solid substrate under various wetting conditions (Kumar *et al.*, 2007).

2.6 Zeta Potential

Zeta Potential (ζ) is the value of an electrical potential difference between the surrounding solution and the layer of solution which attached to the dispersed particles. It has two parts of liquid layer surrounding the particles which are an inner region (Stern layer) where the ions are strongly bound and an outer (diffuse) region where they are less firmly associated. Within the diffuse layer there is a notional boundary inside which the ions and particles form a stable entity. When a particle moves due to gravity, ions within the boundary move it. Those ions beyond the boundary stay with the bulk dispersant. The potential at this boundary is the zeta potential as shown in Figure 2.5.

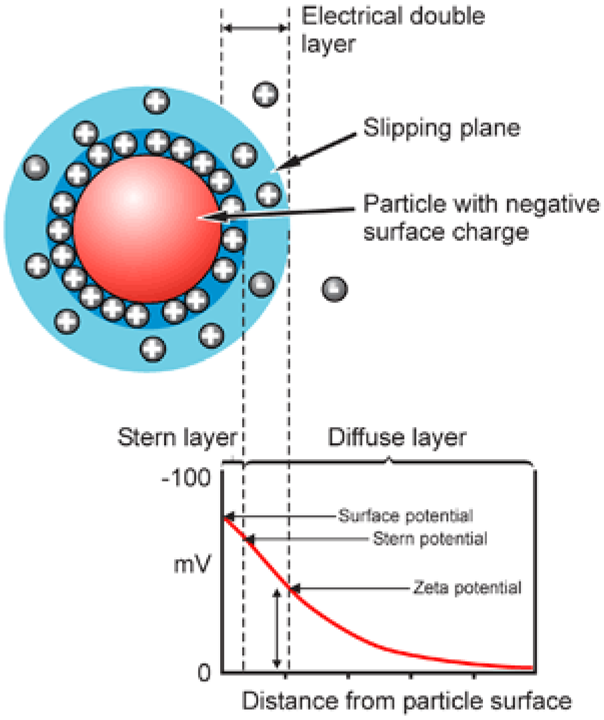
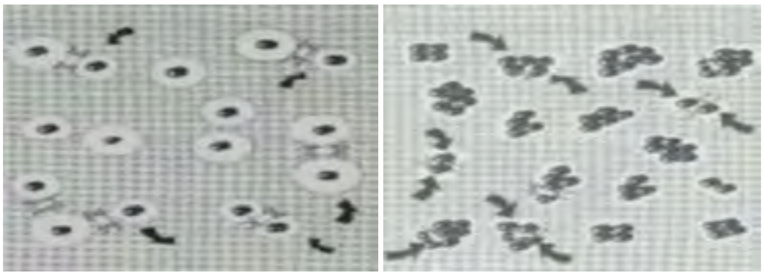


Figure 2.5 Schematic representation of zeta potential.

The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there will be no tendency for the particles to come together. However, if the particles have low zeta potential values then there will be no force to prevent the particles coming together and flocculating as shown in Figure 2.6.



(A) **(B)**

Figure 2.6 A) Well–disperses particles and B) Particle aggregation.

The pH of the sample solution is one of the most important factors that affect its zeta potential. Zeta potential versus pH curve will be positive at low pH and negative at high pH. At the isoelectric point in which the amounts of positive and negative charges are balancing, the zeta potential tends to be zero. There may be a point where the plot passes through zero zeta potential as shown in Figure 2.7.

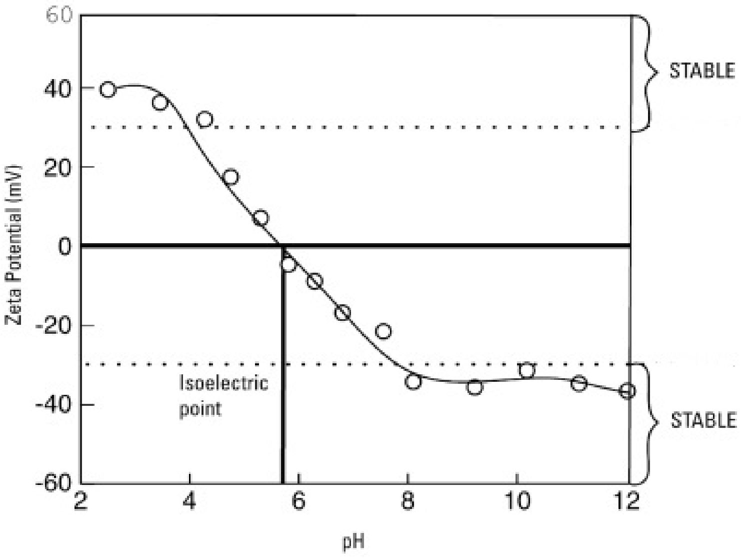


Figure 2.7 A plot of the zeta potential measured as a function of pH.

The thickness of the double layer (κ^{-1}) depends upon the concentration of ions in solution and can be calculated from the ionic strength of the medium. The higher the ionic strength, the more compressed the double layer becomes. The valency of the ions will also influence double layer thickness.

2.7 Dispersion Stability

Dispersion or suspension is an important aspect for the study of colloid science with various applications, from liquid abrasive cleaners, personal care products, ceramic slurries and medicines to paints and inks. Some applications it is necessary to keep the systems well dispersed by repulsive force between charge particles whereas, in others, the systems may be need to aggregate or in terms of their tendency to sediment under the action of gravity. Therefore, dispersion stability is an important component of the detergency system. Solid non-particulate soil was removed from fabric surface as small solid particles suspending into the wash solution. To avoid the soil particles coagulate or aggregation and redeposition, deaggregation of the solid particle is required to achieve a good dispersion by repulsive force between charged particles. Factors affecting dispersion stability are salt concentration, counter-ion valency, zeta potential, and particle size (Cosgrove, 2010).

2.8 Mechanisms of Oily Soil Removal

Several mechanisms in oily soil removal have been desorbed, but the three main mechanisms—roll-up; emulsification, and solubilization—are well-known and accepted (Verma *et al*., 1998; Rosen, 2004).

2.8.1 Roll-up Mechanism

Roll-up or roll-back mechanism is the complete detachment of oily soil from substrate. This can remove oil droplets via two processes; (Figure 2.8) (i) an increase in the contact angle between the oil droplet and the substrate due to the reduction of interfacial tension (IFT) between oil and water, (ii) the occurrence of repulsion force between the head groups of surfactants, adsorbing onto both surfaces of attached oil droplet and substrate.

2.8.1.1 The Increasing Contact Angle Process

This process can be explained by Young's equation as follows;

$$\cos\theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}} \qquad (2.1)$$

where, γ_{SB} = the interfacial tension (IFT) between the substrate and the bath,

γ_{OB} = the interfacial tension (IFT) between the oil and the bath,

γ_{SO} = the interfacial tension (IFT) between the oil and the substrate.

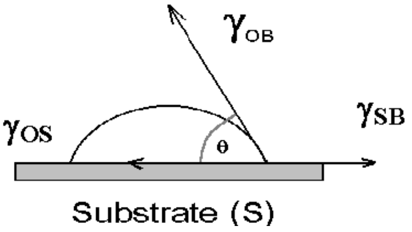


Figure 2.8 The contact angle between an oil droplet and substrate in bath (surfactant solution) (Rosen, 2004).

When surfactants are present in a bath (B) or surfactant solution, surfactant molecules adsorb at two interfaces. As a result, the interfacial tension (IFT) between the substrate and the bath (γ_{SB}) and that between oily soil and bath (γ_{OB}) are reduced causing the decrease in cosθ (or higher θ), so the oily soil will detach from the substrate. Nonetheless, this mechanism will be accomplished when the contact angle is higher than 90°. The higher the contact angle, the easier the soil removed (Broze, 1994). If the contact angle is close to 180° (cosθ=1), the soil will be completely removed. If the contact angle is between 90° and 180°, the soil must be removed by hydraulic current in the bath (Figure 2.9). In contrast, if the contact angle is less than 90°, the soil removal step is not completed, resulting in a remaining fraction of oil on the substrate. Figure 2.9 shows the roll-up mechanism of oily soil removal.

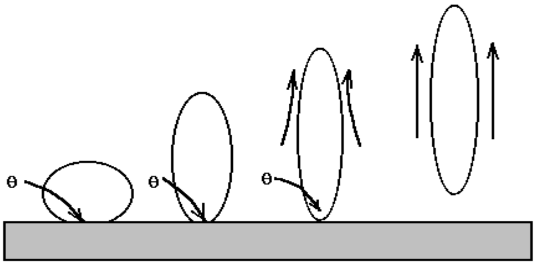


Figure 2.9 Roll-up mechanism with the complete removal of oil droplets from substrate by hydraulic currents (θ> 90°) (Rosen, 2004).

2.8.1.2 Surfactant Head Group Repulsion Process

After the surfactants adsorb at substrate-bath interface (SB) and oily soil-bath interface (OB), the head groups of surfactants which adsorb at the substrate-bath interface will repulse with the head group of surfactants which adsorb onto the oily soil-bath interface. From this repulsion phenomenon, the oil droplet can be detached from the substrate, as shown in Figure 2.10.

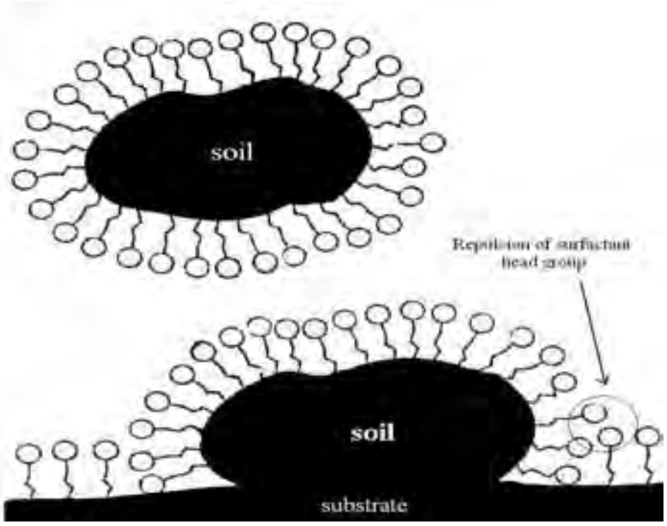


Figure 2.10 Repulsion force of surfactant head groups.

2.8.2 Emulsification Mechanism

Emulsification —snap-off, or necking mechanism— will take place when the contact angle between the oily soil droplet and the substrate is less than 90°. The principle of this mechanism is similar to a roll-up mechanism, but the only difference is the value of contact angle between the oil soil droplet and the substrate. Nevertheless, the disadvantage of this mechanism is the remaining of some residual soil on the substrate due to the fact that the soil/bath interfacial tension is decreased, but the substrate/bath interfacial tension is not change substantially (Figure 2.11).

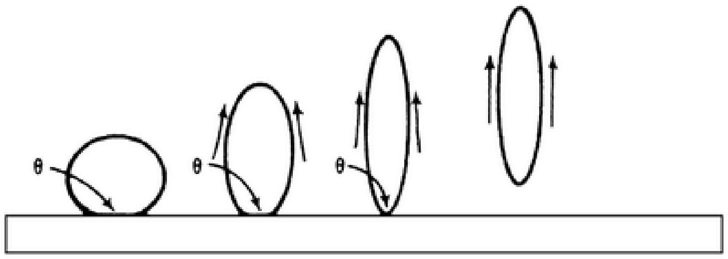


Figure 2.11 Emulsification mechanism to cause partial removal of oil droplets from substrate when θ< 90° (Rosen, 2004).

2.8.3 Solubilization Mechanism

Solubilizaton, or oil uptake capacity, is an oil uptake by moving inside the core of the surfactant micelles. The roles of this mechanism are; (i) to removal small amount of residual oil, which cannot be removed by roll-up or emulsification and (ii) to prevent the redeposition of detached oil on the substrate. The solubilization depends on several factors such as nature of oil and surfactant, surfactant concentration, electrolyte concentration, and temperature. The solubilization becomes substantially high when the concentration of surfactant solution is above the CMC value, where the surfactant forms micelles. The capacity of solubilized oil in the micelle core depends on the chemical structure of surfactant, surfactant concentration, the shape of micelles, and temperature. A very high surfactant concentration (10–100 times of the CMC) leads to a very high amount of oil to solubilize in the micelle core (Schwartz, 1972). The difference between solubilization and emulsification is the thermodynamic stability of keeping all the oily soil from redepositing on the substrate by solubilization, while the emulsification cannot prevent all the redeposition of the detached oil on the substrate (Figure 2.12 and Figure 2.13). The important of solubilization is not only in detergency aspect but also in polymerization, waste water treatment, separation of materials, and so on.

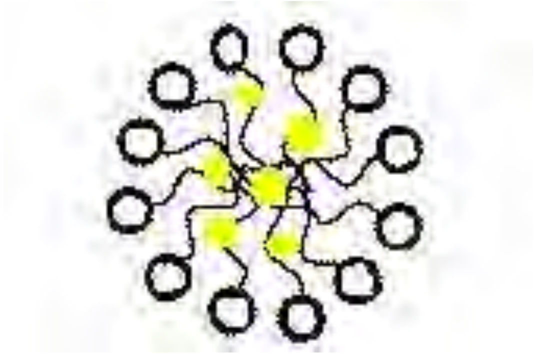


Figure 2.12 Solubilization.

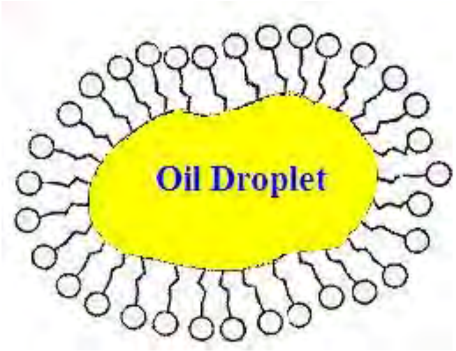


Figure 2.13 Emulsification.

2.9 Soil Redeposition

As the consequences of non-continuous cleaning and washing processes, especially for the batch type, the redeposition of the removed soils is possible for several times. Again, the removed soils from the surface of the substrate will redeposit onto the substrate due to lack of stability of colloid in dispersion. For oily soils removed by solubilization, the process is thermodynamically driven, so that it is essentially a one-way street and re-deposition will be minimal. On the other hand, solid soils cannot be solubilized and redeposition must be slow down by other kinetically controlled means. Emulsified oily soils, where they occur, must be handled similarly. As showed out earlier, one main role of surfactants at interfaces of solid is to increase a degree of colloidal stability to deeply divided particles in aqueous solutions. The adsorption of ionic surfactants at the solid interfaces produces an electrical double layer that retards the approach of the interfaces and prevents or at least hinders redeposition.

2.10 Microemulsions

Microemulsions are an isotropic, thermodynamically stable system which consists of water, oil, and surfactants. These two immiscible liquids can merge into a single phase under appropriate conditions. Under Winsor Type III microemulsion condition, important properties are very high oil solubilization and very low oil-water interfacial tension that is close to zero (Bourrel *et al*., 1998).

Winsor (1954) was the first person to propose 4 basic types of microemulsion as follows;

1. Winsor Type I: Oil-in-water (o/w) microemulsion, defined as oil droplets dispersed in the water phase in equilibrium with an excess oil phase. Most surfactant is soluble in the aqueous phase.

2. Winsor Type II: Water-in-oil (w/o) microemulsion, defined as water droplets dispersing in the oil phase in equilibrium with an excess water phase. Most surfactant is soluble in oil phase.

3. Winsor Type III: This microemulsion type consists of three phases, where the middle phase contains both high contents of oil and water with most surfactants in equilibrium with both excess water and excess oil phases.

4. Winsor Type IV: This type has only one (or single) phase; oil, water, and surfactant are homogeneously mixed in to one phase.

As mentioned above, the phase behaviors of microemulsion systems can also be carried out, known as the phase map or "fish diagram" as illustrated in Figure 2.14. Inside the body of the fish body, the system consists of three phases of excess oil, excess water, and a middle-phase, middle-phase microemulsion has a large solubilization capacity for both oil and water, and ultralow interfacial tension (~10^{-3} mN/m) between the middle-phase microemulsion and the excess oil or water phase. Both high solubilization and ultralow interfacial tension are preferable in many cleaning and environmental remediation applications.

A Winsor Type I microemulsion (oil-swollen micelles) is located on the left hand side of Figure 2.14. In this region, most surfactant solubilizes in water phase to form normal micelles. As a result, oil solubilizes in water. The oil solubilization capacity of Winsor Type I microemulsion is not as high as that of Winsor Type III microemulsion. It is increases when the system approaches the boundary of these two microemulsion systems. Winsor Type I microemulsion can be formulated at low surfactant concentrations, which is generally applied for detergency and soil remediation. Winsor Type II microemulsion locates on the right hand side, where most surfactant solubilizes in oil phase, leading to the formation of reverse micelles. Hence, water is solubilized in the oil phase. Similar to Winsor Type I microemulsion, when Winsor type III microemulsion approaches the boundary between Winsor type III and Type II microemulsions, the solubilization of water in oil increases, corresponding to a decrease in the interfacial tension. The Winsor Type II microemulsion conditions are typically used in dry cleaning to remove hydrophilic particles which cannot be easily removed by organic solvents. At high surfactant concentrations, the solubilization capacity of Winsor Type III microemulsion system surpasses the amounts of oil and water available, yielding a single-phase Type IV microemulsion system that has the same application as Winsor Type III system. The region below the Type III microemulsion is perhaps one of the most intriguing of the phase diagram and it holds the greatest promise for future formulations. In this region, the middle-phase microemulsion does not exist, and there is little oil or water solubilization; however, the ultralow interfacial tension between the oil and aqueous phases can still be achieved (Acosta *et al*., 2008).

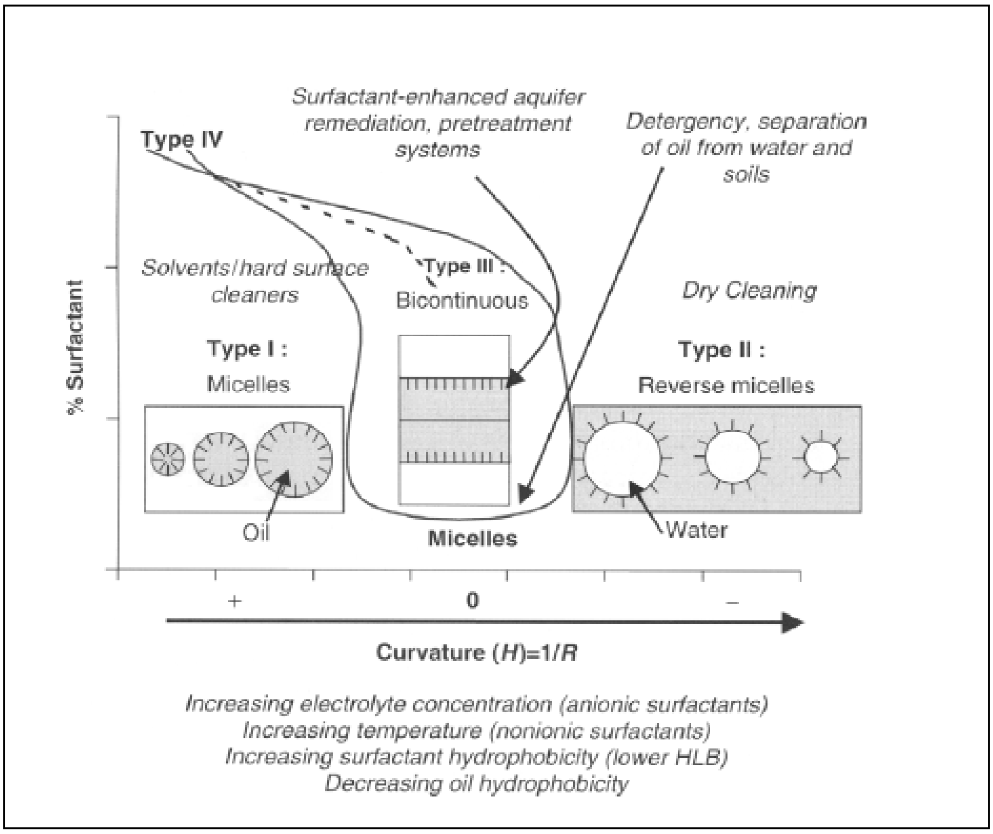


Figure 2.14 Microemulsion phase map. The continuous line indicates the phase boundary between the different microemulsion types (I, III, II, IV). The inset figures show the changes in curvature as the microemulsion transition from Winsor Type I Type III to Type II microemulsion (Acosta *et al*., 2008).

The hydrophile-lipophile balance (HLB) is the one factor that controls the phase transition behaviors and microemulsion formation. The hydrophile-lipophile balance (HLB) is the balance between the hydrophilic (lipophobic) and lipophilic (hydrophobic) portions of surfactant. There are several factors that influence the HLB alteration; (i) the nature of surfactant, (ii) electrolyte concentration or salinity (for ionic surfactant system); if the salinity increases, the HLB will be decreased because the reduction of the electrical interaction of the ionic head group can decrease the surfactant's hydrophilicity or increase the surfactant's lipophilicity, (iii) temperature (most of nonionic surfactant system) if the temperature is raised, the HLB value will be decreased since the increased dehydration of POE chains can increase the lipophilicity, and (iv) co-surfactants or linkers (if a system has two or more two surfactants (which have the different HLB), the HLB of co-surfactants system will be different from the HLB of single surfactant).The phase behavior and the interfacial tension (IFT) as a function of manipulated variables; HLB, salinity, and temperature, are illustrated in Figure 2.15.

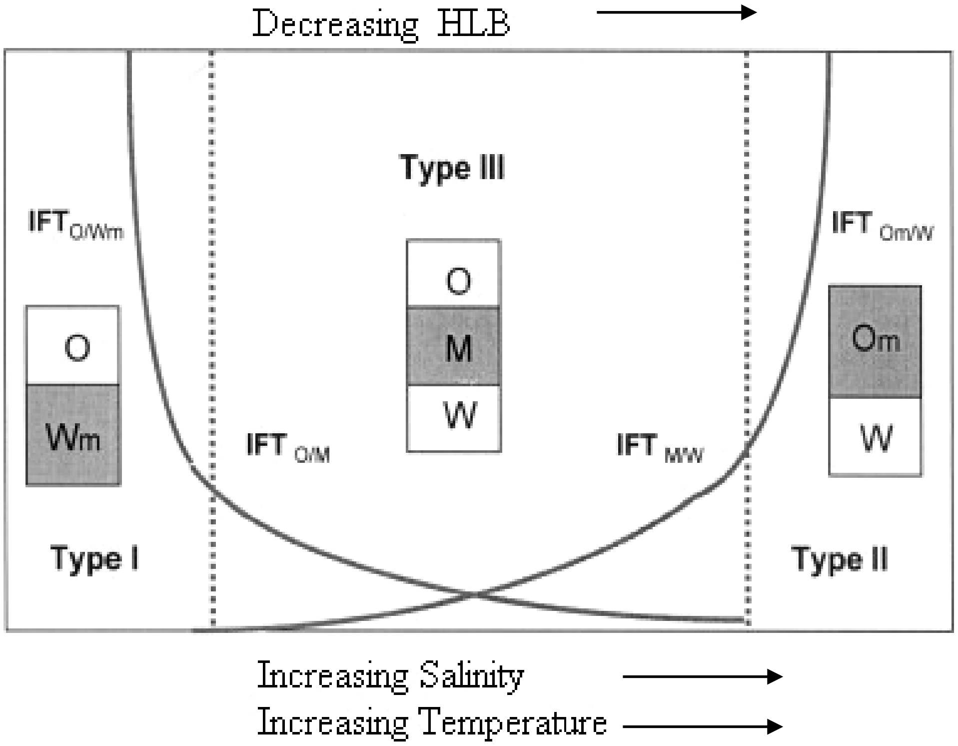


Figure 2.15 Phase behavior and the interfacial tension (IFT) as a function of scanning variables (O is oil; W is water; M is middle phase; Wm is oil-in water (O/W) microemulsions; Om is water-in-oil (W/O) microemulsions) (Tongcumpou *et al.*, 2003).

The phase behavior changes can be estimated from the Winsor R ratio of interactions, which is calculated from Equation.2.2 (Rosen, 2004);

$$R = \frac{A_{CO} - A_{OO} - A_{LL}}{A_{CW} - A_{WW} - A_{HH}} \tag{2.2}$$

where, A_{CO} = the interaction between the surfactant and the oil,

A_{CW} = the interaction between the surfactant and the aqueous phase,

A_{LL} = the self-interaction of the lipophilic portions of the surfactant,

A_{HH} = the self-interaction of the hydrophilic portions of the surfactant,

A_{WW} = the self-interaction in the water phase,

A_{OO} = the self-interaction in the oil phase.

The numerator of the equation represents the net interaction of the lipophilic portion of the surfactant at the interface, and the denominator corresponds to the hydrophilic part of the interface. For R<1, the interface becomes more hydrophilic, and an o/w microemulsion (Winsor Type I) exists. For R>1, the inverse micelles will form, and the solution becomes a w/o microemulsion (Winsor Type II). For R=1, the interactions of the lipophilic and hydrophilic regions are in balance, leading to the optimal formation of a Winsor Type III microemulsion (Bourrel *et al.*, 1998). A single-phase (isotropic) microemulsionis formed under sufficient quantities of amphiphiles (surfactant + alcohol). When R=1, the larger the values of both numerator and denominator, the greater the tendency to form an isotropic system that is called a Winsor Type IV microemulsion system. Moreover, when R=1 and the A_{LL} and the A_{HH} interactions are large, liquid crystals or gels may also form (Rosen, 2004).

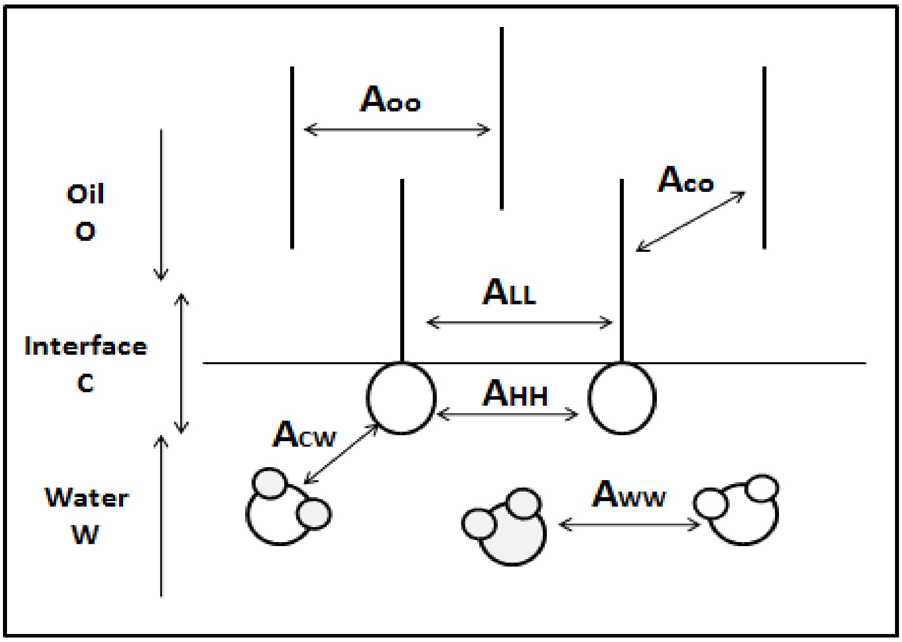


Figure 2.16 The interaction model among the interfacial layer, oil and water phases.

Graciaa *et al.*, (1993) compared the microemulsification of a hydrocarbon oil and polar oil of similar molar volume in different physicochemical environments containing nonionic surfactants with variable alkyl groups in terms of chain's length and size. The results revealed that the length distributions on both hydrophilic and lipophilic groups affected the solubilization. For example, the solubilization of hexadecane showed that with increasing alkyl chain length, the interaction of the surfactant and oil phase (Aco) increased, and had to be compensated by an increase of EON, leading to increases in the Acw. The increases in both Aco and Acw resulted in a large increase in the solubilization parameter.

Komesvarakul *et al.*, (2006) studied the formation of artificial sebum microemulsions with sodium dioctylsulfosuccinatea using a hydrophilic linker (hexylglucocide) and a lipophilic linker (sorbitanmonooleate) with the addition of co-oil. It was found that the mixture of surfactants and linkers could form single-phase triglyceride microemulsions (Winsor Type IV) at room temperature and at low sanility. Furthermore, the added co-oil helped the solubilization of triglycerides at a lower surfactant concentration and reduced the amount of surfactant to form a single-phase microemulsion, which was beneficial for the cosmetic applications.

2.11 Application of Microemulsion for Detergency

Microemulsions have unique properties such as ultralow interfacial tension, large interfacial area, and high capacity to solubilize both water and hydrocarbon compounds. Hence, microemulsion-based formulation becomes a great interest in area of detergency as shown below (Paul and Moulik, 2001).

Tongcumpou *et al*., (2003) studied the relation between microemulsion phase behavior and oil soil detergency. The effects of surfactant composition, temperature, and salinity on detergency performance were investigated, and they found that the transition of microemulsion phases by salt scan technique could be observed for both systems with hexadecane and motor oil. In addition, the use of surfactant mixtures containing both anionic and nonionic surfactants could make the systems become robust with respect to temperature compared to single-surfactant systems, in the supersolubilization or in the Winsor Type III, middle phase, microemulsionregion, detergency performance was much higher than that in either Winsor Type I or Type II microemulsion.

Tongcumpou *et al*., (2006) also studied triolein removal using microemulsion-based formulation with mixed surfactants. The results showed that there were two values of maximum detergency in the range of salinity from 0.1 to 10% NaCl. The higher the hydrophilicity of the system, the higher the salinity required for maximum detergency. The results of the dynamic IFT and the detergency performance from two rinsing methods led to the hypothesis that one of these maxima in detergency results from a spreading or wetting effect. The other maximum in detergency is believed to be related to ultralow IFT associated with oil/water middle-phase microemulsion formation. Triolein removal exceeding 80% was attained, validating the microemulsion approach to detergency.

Phan *et al.,* (2010) examined the use of single extended surfactant in microemulsion-based detergency of vegetable oils. The results showed that good canola oil detergency (>80%) was achieved at 25°C using a single extended surfactant ($C_{14,15}$-8PO-SO_4Na) at a low concentration of 125 ppm. It demonstrates that microemulsion-based extended surfactant formulation was a promising approach for vegetable oil detergency at low temperature.

Tanthakit *et al.,* (2010) studied palm oil removal from fabric using microemulsion-based formulations,where palm oil was chosen asoily soil model in phase studies and detergency tests. The use of an extended surfactant was expected to provide both high oil solubilization and ultralow IFT for the palm oil, which are beneficial to the detergency application. In this study, mixed surfactant systems consisting of $C_{14,15}H_{29,31}(PO)_3SO_4Na$, an anionic extended surfactant abbreviated $C_{14,15}(PO)_3SO_4$, and a secondary alcohol ethoxylate or $C_{12,14}H_{25,29}O(EO)_5H$, a nonionic surfactant abbreviated $C_{12,14}O(EO)_5$, were employed in order to obtain a proper HLB (Hydrophilic-Lipophilic Balance). The oil removal for the surfactant blend could exceed 90%, which was greater than that for either component surfactant alone or for a commercial liquid laundry detergent.

2.12 Factors Affecting Oily Soil Detergency

Linfield *et al*., (1962) reported that agitation speed, washing time, and detergent concentration affected the detergency performance. Webb *et al*., (1998) also suggested that the soil removal from fibrous substrate depended on the nature of the soil, the sequence during application, temperature, and the type of detergent formulation. Germain (2002) conducted the detergency experiment using a tergotometer and were found to several factors such as agitation speed, temperature, and amount of detergent must be strongly affect the detergency performance.

2.12.1 Surfactant System

Obendorf *et al*., (1982) found that the type of surfactant affected the detergency performance. An anionic surfactant was found to remove oil from a cotton fabric more effectively than a nonionic surfactant. As expected, anionic surfactants are effective on more polar fiber. However, there was little or no difference between two detergents in total oil removal from a polyester/cotton fabric.

Solan *et al.*, (1988) studied the effects of nonionic surfactant and temperature on detergency efficiency of non-polar soils (hexadecane, squalene, mineral oil) on a polyester/cotton fabric. It was found that the maximum detergency efficiency corresponded with the phase inversion temperature (PIT). Moreover, they reported that the optimum temperature was increased when the degree of ethoxylation of surfactant increased.

The effect of ethoxylation number in nonionic surfactant to soil removal was also studied by Wormuth *et al*., (1991). They found that the oily soil removal was influenced by the ethoxylation number in nonionic surfactant because when the ethoxylation number of C_{12-14}alkylpolyglycol ether was increased, the solubilization power of surfactant decreased, resulting in the decrease in oily soil removal.

The advantages of using surfactant mixtures were reported by Ogino *et al.,* (1992). They found that mixed surfactant systems generally exerted greater than single surfactant systems for enhancing of solubilization. However, this enhancement did not apply to all mixed systems.

Generally, a surfactant mixture that can exhibit a low oil-water interfacial tension is considered to provide superior oily soil detergency. Verma *et al.* (1998) measured the oil-water interfacial tension for a mixed anionic/nonionic surfactant system (NaLAS/$C_{12}EO_3$ and NaLAS/$C_{12}EO_7$) as a function of temperature and time. The oil-water interfacial tension was found to decrease as a function of time for all blends containing nonionic surfactant. It was proposed that the diffusivity of this hydrophobic fraction into phase lead to a decrease in oil-water interfacial tension. The investigation conducted by Goel also gave similar results. Goel (1998) was reported the optimal EO moles (for maximal detergency) showed a monotonically increasing trend with increasing concentration ratio of nonionic surfactant to anionic surfactant for a fixed level of electrolyte. The optimal EO moles also increased with increasing level of electrolyte in the system. However, the effect of nonionic/anionic ratio was much stronger than the effect of electrolyte on the optimal EO moles. In the same year; Goel investigated detergency performance at different ratios of nonionic to NaLAS surfactant concentrations. He found that the minimum value of interfacial tension (IFT) was a function of EO moles in the nonionic surfactant. These minima of IFT were found to relate to high solubilization of oily soil, corresponding to the maxima in detergency.

In 2003, Tongcumpou *et al.,* found that the microemulsion-based formulation of mixed surfactants of sodium dioctylsulfosuccinate (AOT, a surfactant of intermediate HLB), alkyldiphenyl oxide disulfonate (ADPODS, a very hydrophilic surfactant), and sorbitanmonooleate (Span 80, very hydrophobic surfactant) with motor oil and hexadecane was temperature-insensitive supposed by the results of Salager *et al.*, (1979) and Anton *et al.*, (1992). She also found that interfacial tension (IFT) values under super solubilization (SPS) conditions were not substantially worse than that under the optimal conditions in a Winsor Type III system (middle phase). In other words, quite low IFT could be attained without formation of a middle phase, as suggested by Wu *et al.*, (2000). In addition, the super solubilization region was also found to give oil removal as high as that in the middle phase region. Besides, they found that their microemulsion formation required fairly at high salinity of 16 wt% to achieve the super solubilization.

In 2005, Tongcumpou *et al.*, found that, for their microemulsion-based formulation, the oil removal in the rinse step was as high as that in the wash step for both super solubilization and Winsor Type III regions because during the wash step, the spreading effect can occur, as supposed by other results (Thompson, 1994; Healy *et al.*, 1976). In addition, Tanthakit *et al.*, (2008) found that a mixed surfactant system of 1.5 wt% ADPODS, 5 wt% AOT, and 5 wt% Span 80 exhibited the Winsor Type III microemulsion at low salinity of 2.83 wt%. With this selected formulation, detergency performance increased with increasing active total surfactant concentration.

2.12.2 Nature of Oil

There were a number of research works about polar/non-polar soils removal (Gordon, 1967; Powe, 1963; Morris *et al.*, 1982). A residual oily soil contained a greater percentage of nonpolar components than fresh oily soil while polar soil tended to be more easily removed in the aqueous detergent system. Kissa (1987) also reported that the oil viscosity could affect the oil removal. The oil with lower viscosity was removed from the substrate faster than that with higher viscosity.

Interestingly, the viscosity of the emulsion in used motor oil and the aqueous detergent solution was found to be five times higher than that in the original used motor oil.

The effect of polar soil components on the phase inversion temperature and optimum detergency conditions was also studied by Raney *et al.*, (1987).They proposed that the snap-off of the oil drops resulted from the interfacial tension reduction at the soil/water interface, thus influencing the removal of non-polar/polar soil mixtures. It was also suggested that a minimum quantity of polar material in the soil might be necessary to attain a high soil removal. Chi *et al.*, (1999) found that highly unsaturated oily soil was easily oxidized upon aging, resulting in increasing removal, whereas saturated oil was relatively stable. Nevertheless, the aging made oil particles penetrated deeply into the fabric and fiber structures, resulting in difficulty in removal.

2.12.3 Salt

Oil removal performance in the presence of electrolytes was reported by Webb *et al.* (1987). For the mineral oil, the removal time of the mixed system with 0.5 ml NaCl was about half that of the nonionic alone. Furthermore, they found the addition of the surface active compound led to the significant increase in the interfacial tension of the mixture, and also influenced the oil removal adversely.

The detergent efficiency as a function of salt concentration was found to be independent on temperature (Solan *et al.*, 1992). The detergent efficiency was obtained at the optimum salinity 10of %wt NaCl, which was a favorable condition for microemulsion formation. In 1993, the effects of temperature and salt concentration on the detergency efficiency were investigated by Azemar *et al.*, 1993, and they concluded that detergency efficiency both with and without electrolyte increased with temperature in the same trends and reached an optimum level. However, the optimum temperature for the maximum detergency efficiency was shifted towards lower temperature as the electrolyte concentration increased (less effect of salinity).

2.12.4 Substrate

The performance of soil removal is known to be influenced by the nature of the substrate (Christ *et al.,* 1994). Based on previous observation, Chi (2001) investigated the effect of the substrate on the removal of unaged oily soil and found that the removal efficiency on nylon was higher than that on cotton or polyester. In fact, cotton has high polar characteristic that was responsible for release oily soil fairly well in an aqueous detergent system, but the results did not follow the expectation in this case. In addition, low removal of squalene from cotton was the consequence of morphological characteristics of cotton that made oil difficult to be removed.

Soil removal from cotton fabrics that modified by mercerization and carboxymethylation was studied by Obendorf (2001). It was proposed that the carboxymethylation changed the chemistry of the fiber by increasing the carboxyl group contents. This change was believed to reduce the amount of soil deposited in the lumen of fiber. In the mercerization was indicated that chemical accessibility and hydrophilicity of the fiber structure influenced both soil deposition and soil removal of lipid soil.

2.12.5 Other Factors

In the study of detergency formulation and performance, Linfield *et al*., (1962) purposed that the increase in agitation speed, washing time, and detergent concentration were responsible for the increasing in detergency performance to the maximum level, where their optimum conditions were observed at around 150–170 rpm and at 15–20 min washing time. Moreover, Obendorf *et al*., (1982) reported that the increasing in either mechanical action or detergent concentration led to the increasing in triolein removal, even though the triolein concentration in the cotton fiber was still high. Interestingly, Raney *et al.,* (1987) studied the correlation of PIT and detergency performance. The maximum detergency in ternary system was found to occur when the temperature closed to the PIT of the system, which composed of water, the surfactant and the hydrocarbon soil itself. Webb *et al*., (1988) also implied that a builder was another influenced factor for enhancing the cleaning efficiency.

CHAPTER III
EXPERIMENTAL

3.1 Materials

Methyl palmitate or palmitic acid methyl ester (99.8% purity) is supplied by Sigma-Aldrich (BKK, Thailand). Cotton and polyester were purchased from Test fabrics, Inc. (Middlesex, NJ, USA). The surfactant used in this study was extended surfactants which are a branched alcohol propoxylate sulfate sodium salt with 12 to 13 carbon numbers with approximately four propylene oxide (PO) units ($C_{12,13}$-4PO-SO_4Na) with an active content of 30 wt%, as provided by Sasol North America (Lake Charles, LA) and a sodium linear-alkyl polypropoxylated polyethoxylated sulfate (R-$(PO)_y$-$(EO)_z$-SO_4Na) synthesized and donated by Huntsman Petrochemical Corp (Houston, TX) with 12 to 14 carbons in its hydrophobic tail, 10 and 16 propylene oxides and 2 ethylene oxide groups *with an active content of* 24.2 and 23.3 wt%, respectively. Two nonionic surfactants were evaluated: alcohol ethoxylates (EO9) with a C12 to C14 alkyl chain length and 9 ethylene oxides *with an active content of 99.9 wt% – Thai* Ethoxylate Company Limited (BKK, Thailand), methyl ester ethoxylate (MEE) with a C12 alkyl chain length and 18 EOs *with an active content of* 90.2 wt% – Lion Corporation (Tokyo, Japan). Two anionic surfactants were evaluated: sodium dodecyl sulfate (SDS) *with an active content of* 99 wt% – Sigma-Aldrich (BKK, Thailand) and methyl ester sulfonate (MES) with a C14 alkyl chain length *with an active content of* 99.8 wt% – Lion Corporation (Tokyo, Japan). Sodium mono- and dimethyl naphthalene sulfonate (SMDNS) which has an active content of 45 – 55 %wt as a hydrophilic linker was obtained from CKWitco (Houston, TX).For other chemicals, Oil red O (solvent Red 27, No. 26125) was purchased from Aldrich Chemical Company, Inc. An electrolyte, sodium chloride (NaCl), was perchased from Lab Scan Asia Co.,Ltd. Deionized water is used to prepare all solutions.

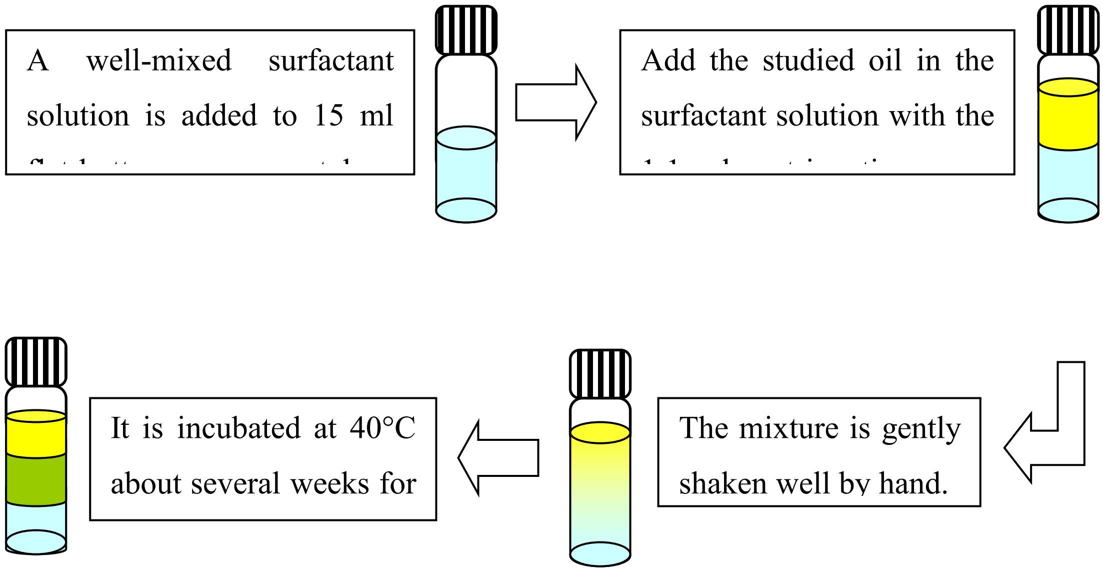
3.2 Experimental Procedures

The experiment part of this research is divided into two parts. The first part is to study the phase behaviors and microemulsion formation and the second part is detergency experiments.

3.2.1 Phase Behavior and Microemulsion Formation

3.2.1.1. Microemulsion Formation

Phase studies are performed by preparing different aqueous surfactant concentrations. The aqueous surfactant solution and oil are equally added to a series of flat-bottomed screw-capped tubes. Samples are gently shaken well and left in a water bath for attainment of equilibrium at 40 °C which can be normally reached within a few days to a week, depending on the combination of the system. The equilibrium state is justified by observing that the volume of each phase in the vial remains unchanged. The schematic of the experiment for microemulsion formation is shown in Figure 3.1.



A well-mixed surfactant solution is added to 15 ml

Add the studied oil in the surfactant solution with the

The mixture is gently shaken well by hand.

It is incubated at 40°C about several weeks for

Figure 3.1 Schematic experiment of microemulsion formation.

3.2.1.2. Fish Diagram Study

The types of microemulsions are classified by the visual observation and used to construct a fish diagram which is a graph to be plotted as surfactant concentration (%wt.) versus sodium chloride concentration (%wt.) at various temperatures. These phase plots are called fish diagrams. The fish diagrams are generally used to determine a minimum surfactant concentration; required to form a Winsor's Type III microemulsions, which is known as the critical microemulsion concentration (CμC). Moreover, the intersection between three microemulsion regions (Winsor's Types I, II, and III) shows the solubilization capacity of the system to obtain a single phase of microemulsion (see in chapter II).

3.2.1.3. Solubilization Parameter or Phase Height

After equilibrium, the height of each liquid phase was measured by using a cathetometer (model TC-II from Titan Tool Supply, Inc. attached to a digital height gauge, model 192-631) is obtained from Mituyo, with an accuracy of 0.001 mm. The solubilization capacities are calculated in terms of the solubilization parameter (SP).

3.2.1.4. Interfacial Tension Measurements

The measurement of interfacial tension (IFT) between the aqueous phase (the surfactant solution) and the oil phase (methyl palmitate) under different surfactant concentrations (0-0.5 wt%) and temperatures (30-50 °C, higher than the melting point of methyl palmitate) were done by using a spinning drop tensiometer (University of Texas, Model 500). A quantity of 1-3μL of methyl palmitate (at above the melting point) was injected into a 300 μL capillary tube filled up with a surfactant solution having different NaCl concentrations. The diameter of oil drop was recorded after 20 min injection, in which corresponded to the time used for the wash step in detergency experiments.

3.2.2 <u>Detergency Experiments</u>

3.2.2.1. Fabric Preparation

The fabric was cut into 3 x 4 inch swatches in a warp and weft direction and pre-wash with DI water to eliminate residues of mill finishing agents that can influence the oil removal results. The pre-washing method is followed the ASTM standard guide D4265-98 (Annual Book of ASTM Standards, 2000).

3.2.2.2. Soiling Procedure

The tested oil is dyed by an oil soluble Oil-Red-O dye using the standard method (Goel, 1998): approximately 0.1 g of the oil-soluble dye in 100 mL of the oil is prepared for use as a colored soil for the detergency experiments. The soiling procedure is done by diluting 10 mL of the clear dyed oil with dichloromethane (or dimethyl chloride) to 100 mL. The fabric is folded and put in a glass container into which the dyed oil solution is poured until the fabric is completely submerged. It is allowed to stand for 5 min. The soiled fabric is then unfolded and laid on a flat plate in a ventilated hood at room temperature overnight in order to dry the soiled fabric. All soiled swatches will be freshly prepared for each set of laundry experiments since a different aging of the soil on the textile has an effect on detergency results.

3.2.2.3. Laundry Procedure

The laundry procedure is carried out by using a terg-o-tometer (Copley, Model DIS 8000), which simulates home washing-machine action in a bench scale unit. The laundry procedure has three steps: first, washing for 20 min; secondly rinse 1 for 3 min and finally rinse 2 for 2 min. DI water is used for both rinses. The volume of both surfactant solution used as washing solution and rinsing water are fixed at 1,000 ml. An agitation speed of every step is fixed at 120 rpm.

3.2.2.4. Oil Removal Measurement

Oil removal is quantified by percentage of oil removal, which is a portion of residual oil on the swatches to be washed during the detergency process. The residual oil will be extracted by submerging a swatch in isopropanol overnight at room temperature, and then the absorbance of the extracted solution will be measured at 520 nm of wavelength by an ultraviolet/visible spectrophotometer

(8452A, Hewlett-Packard). The residual concentration of oil is calculated from the calibration curve of control oil solution, which plots between colored oil concentration and absorbance. The oil removal (%) is obtained from the values of oil levels on the swatch before and after washing.

3.2.2.5. Particle Size Measurement

The Particle size distribution of methyl palmitate particles suspended in the washing solution after the wash step at 20°C was measured by a particle size analyzer (Malvern, Mastersizer X).

3.2.2.6. Surface Tension Measurement

The surface tension of a surfactant solution with varying surfactant and NaCl concentrations was measured by a Wilhelmy plate tensiometer (Krüss, K100) at different temperatures. The inflection point of the plot of surface tension versus the log of initial surfactant concentration was used to determine the critical micelle concentration (CMC).

3.2.2.7. Contact Angle Measurement

A 2 µL drop of a surfactant solution with different NaCl concentrations and different surfactant concentrations was placed on the methyl palmitate surface by using a micro-syringe and the contact angle was measured after 30 s by a contact angle measuring instrument (Krüss, DSA 10 Mk2) using the sessile drop technique. During the measurement, the sample chamber was kept at 25°C in order to prevent melting of the sample (methyl palmitate).

3.2.2.8. Oil Solubilization Measurement

An excess amount of methyl palmitate was added to a surfactant solution having a different surfactant and NaCl concentrations at different temperatures. The solution was stirred at 120 rpm for 20 min. The surfactant solution phase of the mixture was filtered and the filtrate was measured for total carbon concentration of the dissolved methyl palmitate plus the surfactant by a total organic carbon analyzer (TOC) (Shimadzu, TOC 5000). The TOC concentration of dissolved methyl palmitate was obtained by subtracting the total TOC value with the TOC value of surfactant. The solubility of methyl palmitate obtained was then subtracted from the oil removal to determine the portion of unsolubilized (dispersed or emulsified) methyl palmitate. The measurement time of 20 min was selected to be the same as the wash step time used in the washing experiments. In addition, the oil solubilization measurement was also carried out with varying time until each system reached a maximum or equilibrium solubilization level which was found at around 24 h for all studied systems.

3.2.2.9. Oil Dispersion stability Measurement

The dispersion stability of methyl palmitate solid particles having average diameters of 100 μm suspending in DI water or an surfactant solution with different NaCl concentrations at 25 °C (below the melting point) was determined by measuring absorbance as a function of time using a UV–Visible spectrophotometer (Hewlett-Packard, 8452A). The solution was prepared by adding the methyl palmitate particles in the surfactant solution, after being well mixed; the prepared solution was transferred to a spectrophotometer cuvette. The reading of absorbance at a wavelength of 550 nm was recorded every 10 s for 2 h. The absorbance values in the range of 2000 – 5000 s were averaged to represent the dispersion stability. The higher the absorbance, the higher the dispersion stability.

3.2.2.10. PZC Measurement

A powder sample of methyl palmitate or cotton or polyester fabric was added into distilled water at different solution pH values using a 0.1 M HCl or 0.1 M NaOH solution for pH adjustment. After that, the solution with any added powder sample was kept at 20 °C for 24 h. The initial pH value of this solution, prior to adding the powder sample and the final pH after 24 h were measured by a pH meter (Ultra basic DENVER Instrument). The point of the intersection of the initial and the final pH lines was used to indicate the point of zero charge (PZC) of each material.

3.2.2.11. Zeta Potential Measurement

About 3.5 mg of methyl palmitate powder was added into a solution having different surfactant and NaCl concentrations. The mixture was stirred and kept at 20 °C for 24 h. Subseqently, the solution was transferred to an electrophoretic cell of a zeta meter (Zeta-Meter 3.0+) equipped with a microscope module. After applying a suitable voltage, the charged particles moved towards the electrode having opposite charge until attaining a steady state (the particles moved with a constant velocity). The velocities were measured and averaged and referred to as electrophoretic mobility which was calculated by the zeta meter instrument automaticall.

3.2.2.12. Scanning Electron Microscope (SEM) Images

The physical feature of studied fabrics before and after soiling with methyl palmitate and washing at the studied conditions was investigated by using scanning electron microscope, SEM (HITACHI, TM3000).

CHAPTER IV

LAUNDRY DETERGENCY OF SOLID NON-PARTICULATE SOIL OR WAXY SOLIDS: PART I. RELATION TO OILY SOIL REMOVAL ABOVE THE MELTING POINT

4.1 Abstract

In this work, methyl palmitate or palmictic acid methyl ester, a monoglyceride, was used as both a model solid fat below the melting point and as an oily soil above the melting point. An anionic extended surfactant [branched alcohol propoxylate sulfate sodium salt (C_{123}-$(PO)_4$-SO_4Na)] was used to remove methyl palmitate from cotton and from polyester. Above the melting point (~30 ºC) of methyl palmitate, the maximum oily soil removal was found to correspond to the lowest dynamic interfacial tension (IFT), as is common with liquid soils. Below the melting point, the lower the contact angle of the wash solution against the soil (indicating higher wettability), the higher the solid fat soil detergency. The removed methyl palmitate was found to be mostly in unsolubilized droplets or particles with a small fraction of micellar solubilization for both solid and liquid forms. The presence of surfactant can prevent the agglomeration of detached methyl palmitate particles in both liquid and solid forms, reducing redeposition and enhancing detergency. Below the melting point, the surfactant aids the solution wetting the surfaces, then penetrating the waxy solid, causing detachment as small particles, and dispersion of these particles. Unlike particulate soil detergency, electrostatic forces are not the dominant factor in fatty soil detergency.

Keywords Solid non-particulate soil, Solid fat soil, Methyl palmitate, Extended surfactant, Laundry detergency

4.2 Introduction

In laundry detergency, several factors affect the performance such as nature of soils, the properties of surfactant, nature of solid surface, mechanical action applied during washing, water hardness, washing temperature, electrolyte level, and additives (e.g., builder, enzyme, and anti-redeposition agent) [1-5]. The previous work on oily soil detergency using different liquid oils demonstrated good correlation between detergency efficiency and interfacial tension (IFT) between the oil and the water bath [6-13]. Recently, our research group has published studies of the mechanisms of particulate soil detergency using carbon black as a model hydrophobic soil and kaolinite and ferric oxide as model hydrophilic soils. It was found that electrostatic forces dominate soil removal, even for nonionic surfactants and hydrophobic fabric [14, 15].

Solid non-particulate soil or solid fat soil is a separate class of contaminants which has properties of liquid and/or solid, depending on temperature. Practical examples of such soils are butter, sebum from human skin, or solidified hamburger or bacon grease. These soils are particularly challenging to remove in low temperature laundry detergency, which is a current topic of great interest due to energy savings and fabric damage at high temperatures. Often, soils are mixtures between liquid and solid fat soils in which the liquid oil is entrapped in the crystal structure of solid oil under a moderate temperature, causing it to be hard to remove. Despite the importance of this soil removal in practical detergency, there are few literature studies of solid fat soil detergency. Scheuing [16] studied the detergency mechanism of tristearin (model solid fat soil) by using Fourier transform infrared spectroscopy (FT-IR) and reported that the removal of solid triglycerides from a fabric surface was more complex than solid hydrocarbon soils because of the polymorphism in the crystal structure of tristearin. Powe [17] studied detergency of different hydrocarbon soils, and found that a maximum removal of each solid fat soil was somewhere near its melting point. Kawase et al. [18, 19] studied the removal mechanism of solid fatty acid soil by using nonionic and anionic surfactants and they reported that solubilization was the dominant mechanism at low temperatures.

An extended surfactant has a group of intermediate polarity, such as polypropylene oxide (PO) or polypropylene-polyethylene oxide (PO-EO) group, inserted between the hydrophilic head and hydrocarbon tail group. As a result of this unique structure, extended surfactants can further extended into both oil and aqueous phases, resulting in a smoother transition between the hydrophobic and hydrophilic regions at the interface. The presence of a polypropylene oxide group in the hydrocarbon tail of the surfactant molecule helps extend the tail to an oil phase, while still maintaining good interaction with the water phase. Hence, use of an extended surfactant can facilitate the formation of a middle-phase microemulsion, which provides both high solubilization and ultralow interfacial tension (IFT), leading to various applications such as extraction, separation, and textile cleaning [20-23]. Phan et al. [24] examined the use of a single extended surfactant in detergency of vegetable oils. High canola oil detergency (> 80%) was achieved using a single extended surfactant ($C_{14,15}$-8PO-SO_4Na) at concentrations as low as 125 ppm and a temperature of 25 ^oC. Tanthakit et al. [8] studied palm oil removal from fabric using microemulsion-based formulations of a mixture of an extended surfactant ($C_{14,15}$-3PO-SO_4Na) and a nonionic secondary alcohol ethoxylated surfactant ($C_{12,14}$-$O(EO)_5$) at a 25:75 weight ratio. The oil removal for this surfactant blend could exceed 90 %, which was greater than those of any single surfactant alone and of a commercial liquid laundry detergent. Do et al. [25] reported that the mixture of a linear extended surfactant (C_{10}-18PO-2EO-SO_4Na) and a hydrophobic twin-tailed sodium dioctylsulfosuccinate surfactant showed synergism in a Winsor Type III microemulsion formulation, leading to high detergency of vegetable oils and semi-solid fats at low salinity and a low washing temperature.

In this paper, methyl palmitate or palmitic acid methyl ester, a monoglyceride, with a melting point around 30 °C, was used as a model single component solid fat or oily soil being removed from either hydrophilic surface (cotton fabric) or hydrophobic surface (polyester fabric) by using a single anionic extended surfactant at temperatures both higher and lower than the soil's melting point. Other fundamental physical properties of the system were studied to better understand the forces involved in soil removal and help guide future development of cold water detergent formulations.

4.3 Experimental Procedures

4.3.1 Materials

Methyl palmitate or palmitic acid methyl ester (99.8% purity) and Oil red O (solvent Red 27, No. 26125) were supplied by Sigma-Aldrich (BKK, Thailand). Cotton and polyester were purchased from Test fabrics, Inc. (Middlesex, NJ, USA). The surfactant used in this study was an extended surfactant which is a branched alcohol propoxylate sulfate sodium salt with 12 to 13 carbon numbers with approximately four propylene oxide (PO) units ($C_{12,13}$-4PO-SO_4Na) with an active content of 30 wt%, as provided by Sasol North America (Lake Charles, LA). Sodium chloride (NaCl), dichloromethane, and isopropanol, all analytical grade, were purchased from LabScan Asia Co.,Ltd. De-ionized (DI) water was used to prepare all solutions.

4.3.2 Fabric Pretreatment and Soiling Procedure

Pre-washing of the test fabrics was done using de-ionized (DI) water to eliminate all residues of mill-finishing agents. The pre-washing method followed the ASTM standard guide D4265-98 [26]. After that, the fabric was cut into 3 x 4 inch swatches in a warp and weft direction. Approximately 0.1 g of the oil-soluble dye was added to 100 mL of the oil above its melting point. The colored oil was filtered until clear. Next, 10 mL of the clear dyed oil was diluted with dichloromethane to 100 mL [27]. The swatches were folded and completely submerged in the diluted dyed oil solution for 5 min. The soiled fabrics were then unfolded and laid on a flat glass plate in a ventilated hood at room temperature (25 °C) overnight in order to dry the soiled swatches. All swatches were freshly prepared for each batch of laundry experiments. By this soiling method, the average weight ratios of oil-to-fabric were approximately 0.20±0.01:1 for the cotton and 0.15±0.01:1 for the polyester.

4.3.3 Laundry Experiments

The laundry experiments were conducted using a terg-o-tometer (Copley, DIS 8000), which simulates a home washing-machine action in a bench scale unit. The experimental procedure consisted of a wash step for 20 min with 1000 mL of a surfactant washing solution and two rinse steps for 2 and 3 min with 1000 mL of DI water. An agitation speed for each step was fixed at 120 rpm. Three soiled swatches and one unsoiled swatch for anti-redeposition testing were washed in each bucket for one cycle for replication.

4.3.4 Oil Removal Measurement

Oil removal was quantified based on residual oil on the swatches after washing. The residual oil was extracted by submerging a swatch in isopropanol for 24 h at room temperature, and then the extracted solution was analyzed by an ultraviolet/visible spectrophotometer (Hewlett-Packard, 8452A) [9, 27]. The oil removal was calculated from subtracting the remaining oil residue after washing from the original oil content in each swatch.

4.3.5 Surface Tension Measurement

The surface tension of a surfactant solution with varying surfactant and NaCl concentrations was measured by a Wilhelmy plate tensiometer (Krüss, K100) at two different temperatures (25 and 35 ºC). The inflection point of the plot of surface tension versus the log of initial surfactant concentration was used to determine the critical micelle concentration (CMC) [28].

4.3.6 Particle Size Measurement

The Particle size distribution of methyl palmitate particles suspended in the washing solution after the wash step at 20°C was measured by a particle size analyzer (Malvern, Mastersizer X).

4.3.7 Contact Angle Mearsurement

A 2 μL drop of a surfactant solution with different NaCl concentrations and two surfactant concentrations of 0.1 and 0.3 wt% was placed on the methyl palmitate surface by using a micro-syringe and the contact angle was measured after 30 s by a contact angle measuring instrument (Krüss, DSA 10 Mk2) using the sessile drop technique. During the measurement, the sample chamber was kept at 25°C in order to prevent melting of the sample (methyl palmitate).

4.3.8 Oil Solubilization Measurement

An excess amount of methyl palmitate was added to a surfactant solution having a surfactant concentration of 1000 mg/L (10 times CMC) with 5 wt% NaCl or a surfactant concentration of 3000 mg/L (30 times CMC) with 1 or 5 wt% NaCl at different temperatures. The solution was stirred at 120 rpm for 20 min. The surfactant solution phase of the mixture was filtered and the filtrate was measured for total carbon concentration of the dissolved methyl palmitate plus the surfactant by a total organic carbon analyzer (TOC) (Shimadzu, TOC 5000). The TOC concentration of dissolved methyl palmitate was obtained by subtracting the total TOC value with the TOC value of surfactant. The solubility of methyl palmitate obtained was then subtracted from the oil removal to determine the portion of unsolubilized (dispersed or emulsified) methyl palmitate. The measurement time of 20 min was selected to be the same as the wash step time used in the washing experiments. In addition, the oil solubilization measurement was also carried out with varying time until each system reached a maximum or equilibrium solubilization level which was found at around 24 h for all studied systems.

4.3.9 Interfacial Tension Measurement

The measurement of dynamic interfacial tension (IFT) between the aqueous phase (the surfactant solution) and the oil phase (methyl palmitate) for varying surfactant concentrations and temperatures (higher than the melting point of methyl palmitate) was conducted using a spinning drop tensiometer (University of Texas, Model 500). A volume of 1-3 μL of methyl palmitate (above the melting point) was injected into a 300 μL capillary tube filled up with a surfactant solution having different NaCl concentrations and two surfactant concentrations of 0.1 and

0.3 wt%. The diameter of the oil drop was recorded 20 min after injection, which corresponded to the time used for the wash step in detergency experiments.

4.3.10 Oil Dispersion Stability Measurement

The dispersion stability of methyl palmitate solid particles having average diameters of 100 μm suspending in DI water or an aqueous solution containing 0.1 or 0.3 wt% surfactant with different NaCl concentrations at 25 °C (below the melting point) was determined by measuring absorbance as a function of time using a UV–Visible spectrophotometer (Hewlett-Packard, 8452A). The solution was prepared by adding the methyl palmitate particles in the surfactant solution, after being well mixed; the prepared solution was transferred to a spectrophotometer cuvette. The reading of absorbance at a wavelength of 550 nm was recorded every 10 s for 2 h. The absorbance values in the range of 2000 – 5000 s were averaged to represent the dispersion stability. The higher the absorbance, the higher the dispersion stability.

4.3.11 PZC Measurement

A powder sample of methyl palmitate or cotton or polyester fabric was added into distilled water at different solution pH values using a 0.1 M HCl or 0.1 M NaOH solution for pH adjustment. After that, the solution with any added powder sample was kept at 20 °C for 24 h. The initial pH value of this solution, prior to adding the powder sample, and the final pH after 24 h were measured by a pH meter (Ultra basic DENVER Instrument). The point of the intersection of the initial and the final pH lines was used to indicate the point of zero charge (PZC) of each material.

4.3.12 Zeta Potential Measurement

About 3.5 mg of methyl palmitate powder was added into a solution having 0.1 wt% surfactant and different NaCl concentrations. The mixture was stirred and kept at 20 °C for 24 h. Subseqently, the solution was transferred to an electrophoretic cell of a zeta meter (Zeta-Meter 3.0+) equipped with a microscope module. After applying a suitable voltage, the charged particles moved towards the electrode having opposite charge until attaining a steady state (the particles moved with a constant velocity). The velocities were measured and averaged and referred to as electrophoretic mobility which was calculated by the zeta meter instrument automatically [29].

4.4 Results and Discussion

4.4.1 Detergency Performance: Optimum Concentrations of Surfactant and NaCl

As shown in Table 4.1, added surfactant or NaCl has a negligible effect on the melting point of methyl palmitate (we use 30 °C throughout this paper).

Table 4.1 Melting point of methyl palmitate in various washing solutions

Solution	Melting point (°C)
Only methyl palmitate	27.5 – 29
De-ionized water	28.0 – 29
Surfactant (without NaCl)	
Surfactant (with NaCl)	

Figure 4.1 shows the oil removal and oil redeposition as a function of surfactant concentration and salinity for cotton and polyester at 35 °C and 25 °C in which methyl palmitate is in a liquid form and solid form, respectively. At 35 °C, for any given NaCl concentration, with increasing surfactant concentration, the oil removal increased and leveled off for both test fabrics. For any given surfactant concentration, the oil removal reaches a maximum at 5 wt% NaCl as shown in Figure 4.1(a-1) and (b-1). At 25 °C, the oil removal gradually increases with increasing surfactant concentration and the oil removal reaches a maximum at 1 wt% NaCl as shown in Figure 4.1(c-1) and (d-1). In this work, the ability of low extended surfactant concentration to achieve good detergency is consistent with results of previous studies [23, 24]. Figure 4.1 also shows the effects of salinity and surfactant

concentration on the oil redeposition on cotton and polyester at 35 °C and 25 °C. The amount of oil redepositing on both fabrics decreased with increasing surfactant concentration and leveled off at a high surfactant concentration, depending on the concentration of added NaCl. For any fixed surfactant concentration, the oil redeposition reached a minimum value at 5 and 1 wt% NaCl at 35 °C and 25 °C, respectively. The maximum oil removal with the lowest oil redeposition was found at the same surfactant concentration and salinity for both test fabrics and for both washing temperatures.

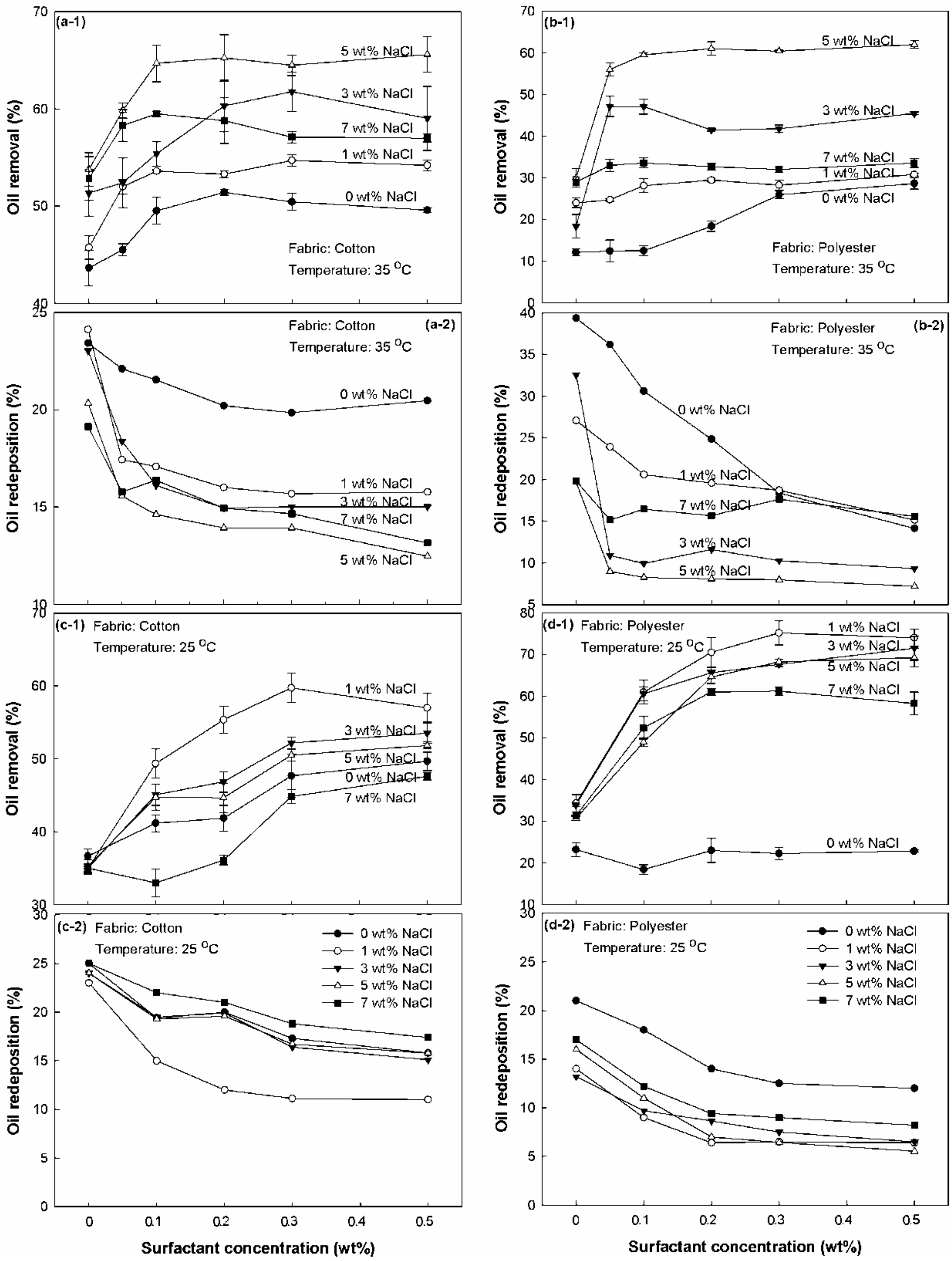


Figure 4.1 Oil removal and redeposition of methyl palmitate as a function of surfactant concentration and salinity on both test fabrics (cotton and polyester) at 35 °C and 25 °C.

4.4.2 CMC Results

The CMC values of the extended surfactant with different NaCl concentrations at 25 and 35 °C are shown in Figure 4.2a. Increasing electrolyte NaCl concentration causes the CMC to decrease due to decrease of the absolute value of the electrical potential at the micelle surface and lower electrostatic repulsion between surfactant head groups at the micelle surface [20, 23]. Moreover, the CMC values were relatively independent of temperature (those at 25 ºC were slightly higher than those at 35ºC for all NaCl concentrations), consistent with low temperature dependence of CMC on temperature for anionic surfactants [30]. The CMC data from Fig.4.2a are plotted as the logarithm of critical micelle concentration vs. logarithm of total concentration of counterion in the solution at the CMC (from added NaCl and surfactant) as shown in Fig.4.2b. This log-log plot is linear and known as the Corrin- Harkins plot [31]. The absolute value of the slope from these plots is the fractional counterion binding to micelles and at 25 °C is 0.29 and at 35 °C is 0.30. These values are only about half of those measured for other ionic surfactants [32, 33], so extended surfactants show unusual electrostatic properties, probably having to do with the packing of the head groups at the micelle surface. In common with other ionic surfactants, fractional counterion binding on micelles has only slight temperature dependence.

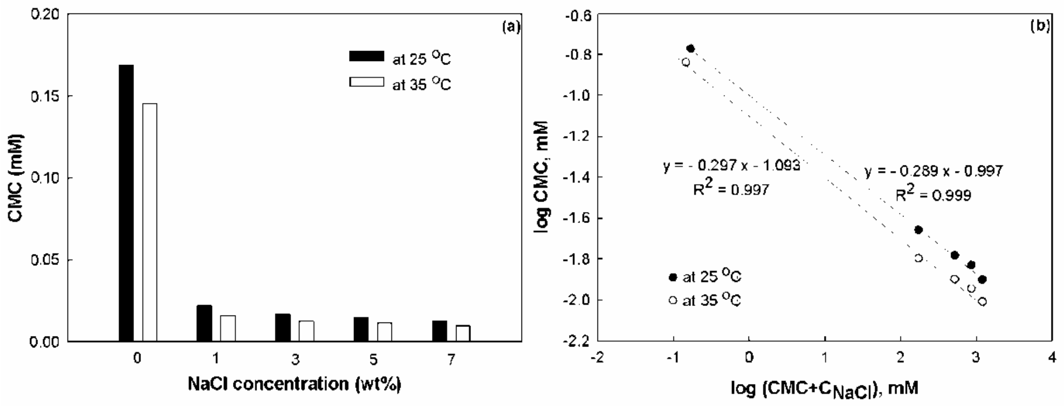


Figure 4.2 (a) Critical micelle concentration (CMC) of $C_{12,13}(PO)_4SO_4Na$ at 25 °C and 35 °C and (b) Corrin and Harkins plot of $C_{12,13}(PO)_4SO_4Na$ from CMC data at 25 °C and 35 °C.

4.4.3 Interfacial Tension (IFT) Results

Figure 4.3 shows the IFT at the interface of the liquid methyl palmitate and surfactant solution as a function of salinity for two surfactant concentrations of 0.1 and 0.3 wt% at 35°C. The IFT values of the surfactant solution and the liquid oil were measured at 20 min, which is long enough for equilibration [34] and corresponds to the wash step time used in the washing experiments. For both studied surfactant concentrations, all of the surfactant solution-oil IFT values measured (0.0172-0.2773 mN/m) are considered to be in the low and ultralow ranges, except at 0 wt% NaCl (2.39 mN/m) which agree well with the measured IFT values between an extended surfactant and canola oil [24, 34, 35]. All of the measured IFT values were much lower than the deionized water-oil IFT value (7.86 mN/m) and the 5 wt% NaCl deionized water-oil IFT value (7.29 mN/M).

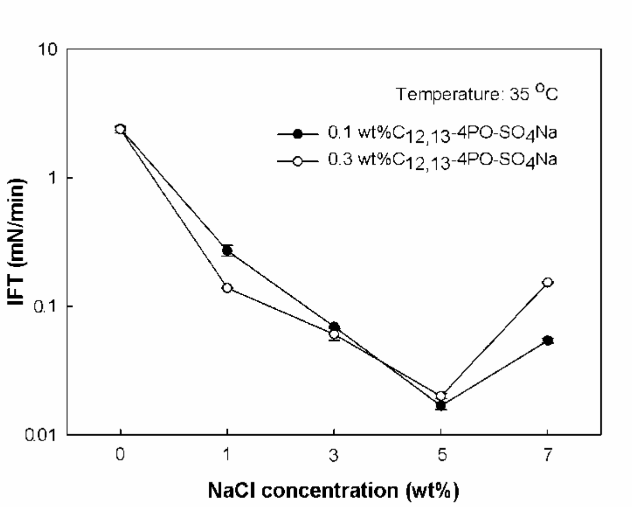


Figure 4.3 The correlation of equilibrium IFT using 0.1 and 0.3 wt%$C_{12,13}(PO)_4SO_4Na$ as a function of salinity at 35 °C.

4.4.4 Contact Angle Results

The contact angle is a physical parameter indicative of how well an applied solution wets a surface. The wetting is a first step of the complex process of detergency. Figure 4.4 shows the contact angles of both 0.1 and 0.3 wt% surfactant solutions on the solid surface of methyl palmitate as a function of NaCl concentration at 25 °C. The contact angle decreases with increasing NaCl concentration and reaches a minimum value (indicating maximum wettability) at a NaCl concentration of 5 wt% and 1 wt% for 0.1 and 0.3 wt% surfactant concentrations, respectively. An increase in surfactant concentration from 0.1 to 0.3 wt% could reduce the best NaCl concentration studied for detergency performance from 5 to 1 wt%. This surfactant concentration increase to 0.3 wt% also resulted in a decreased contact angle from 38° to 33° at 5 and 1 wt% NaCl, respectively. So, wettability may be a factor in detergency and the simple contact angle measurement may be predictive of cleaning efficiency which would be helpful in formulation development.

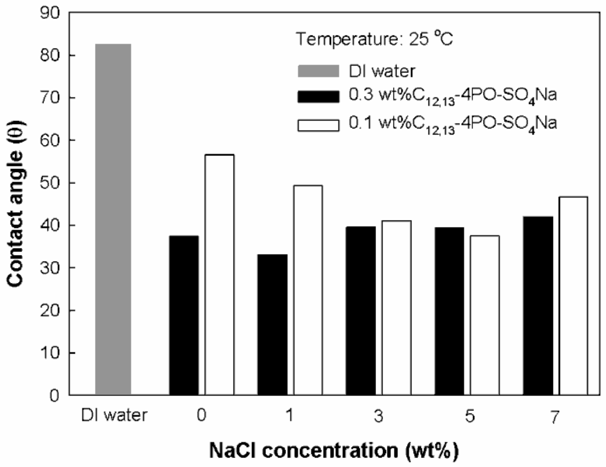


Figure 4.4 Contact angle of 0.1 and 0.3 wt% surfactant solution on methyl palmitate surface at 25 °C as a function of salinity.

4.4.5 Effects of Fabric Types and Washing Temperature on Detergency Performance

Figure 4.5 shows the effect of washing temperature on oil removal and oil redeposition for polyester and cotton fabrics in surfactant solutions of 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ with 1 and 5 wt% NaCl concentrations and of 0.1 wt% $C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl concentration. The washing temperature range of 15 – 50 °C was studied in order to cover both solid and liquid states of methyl palmitate (melting point of 30 °C). The oil removal increased with increasing wash temperature for both studied fabrics using the washing solution containing 0.3 and 0.1 wt% surfactant with 5 wt% NaCl concentrations. The detergency performance on the cotton was slightly higher than that on the polyester fabric for any wash temperature. For the washing solution having 0.3 wt% surfactant and 1 wt% NaCl, the detergency performance on the cotton fabric reached a maximum level around the soil melting point (30 ºC), but did not change substantially with temperature above the melting point. For polyester fabric with the washing solution of 0.3 wt% surfactant and 1 wt% NaCl, the oil removal increased with increasing washing temperature from 15 to 25 ºC. However, detergency decreased dramatically as temperature increased further from 25 to 30 ºC. After reaching this minimum oil removal at the melting point, detergency slightly increased as temperature increased further beyond the melting point. This somewhat surprising minimum in detergency is confirmed by photographs of washed polyester at different washing temperatures shown in Fig.4.6.

For all surfactant systems on cotton and two of the three systems on polyester, oil removal generally increases with increasing temperature which is generally true in detergency of different soils. However, this temperature inversion effect has been previously observed on hydrophobic fabric. Morris and Prato [3] found that the best removal of particulate and oily soil from cotton fabric was at high temperatures, whereas the nonpolar fraction of oily soil removed from polyester was better at low wash temperature. Illman et al. [36] and Gordon et al. [37] found that nonpolar sebum was better removed from Dacron or Nylon in cold water than hot water. This was attributed to the diffusion of liquid oil into the interior of polyester at high temperatures, causing the oil to have poor contact with the surfactant solution [38].

In our study, the soil was dissolved in a volatile solvent, the fabric immersed in the solvent/soil mixture, then the solvent evaporated at 25 °C, below the oil melting point. So, when the soil was deposited on the fabric upon evaporation of the solvent, it was a solid. It was suspected that this solid did not incorporate itself into the fabric fibers as a liquid soil would. So, in separate experiments, after the soiling procedure, each fabric was heated up to 40 °C so the soil became liquefied and could diffuse/imbibe into the fabric weave, then cooled to the temperature of the detergency experiment. As shown in Table 4.2, below the melting point, the oil removal was lower than with normal soiling procedures but at a high wash temperature, detergency was increased around 10%. We conclude that if the soil is a liquid without solvent and allowed to contact the hydrophobic fabric before the system is cooled, as would be the case with sebum and warm hamburger/bacon grease, below the melting point, it is much more difficult to remove the soil than if the soil only contacts the fabric as a solid below the melting point. That this effect is only observed on hydrophobic polyester fabric and not on cotton indicates that the hydrophobic monoglyceride soil has a much stronger attractive interaction with the hydrophobic fabric than a hydrophilic fabric. A broader range of soil polarities would need to be studied to determine the generality of this effect and if monoglycerides/triglycerides are peculiar in their interaction with polyester compared to say hydrocarbon soils. And the temperature inversion effect is not observed for every surfactant system (one out of three here). So, it is recommended that a systematic soiling procedure be used for studies of waxy solids when temperature ranges below the melting point are included.

In a comparison of the two NaCl concentrations in the 0.3 wt% surfactant solution (Figure 4.5), for any studied fabric, the detergency performance at 5 wt% NaCl was higher than that at 1 wt% NaCl at a washing temperature above the melting point due to the low IFT values of 0.009–0.09 mN/m at 5 wt% NaCl as compared to those of around 0.1 mN/m at 1 wt% NaCl (Figure 4.3). In contrast, for any washing temperature below the melting point of 30 ºC, the oil removal at 5 wt% NaCl was lower than that at 1 wt% NaCl, especially on the polyester fabric. The oil removal on the cotton fabric was higher than that on the polyester fabric under studied conditions except at washing temperatures below the melting point with the NaCl concentration of 1 wt%. There is apparently a high affinity of the liquid methyl palmitate and hydrophobic polyester as compared to that on the hydrophilic cotton fabric. However, at a temperature lower than the melting point, the oil removal for the polyester fabric was much higher than that on the cotton fabric, suggesting that the contact of the solid methyl palmitate with the fabric is less than for liquid methyl palmitate. This supports the same conclusion reached from different soiling procedures about solid soil not interacting well with polyester.

The use of surfactant showed a much higher oil removal at any washing temperature as compared to DI water. For DI water systems, the oil removal slightly increased and reached a maximum level at about the melting point for both test fabrics. Beyond the melting point (30 ºC), the oil removal on polyester fabric slightly decreased with further increasing washing temperature. Therefore, the best conditions found at any temperature below the melting point were a 0.3 wt% surfactant concentration with a 1 wt% NaCl concentration whereas the same surfactant concentration of 0.3 wt% and 5 wt% NaCl were found to be better for a washing temperature above the melting point. Generally, it is known that an increase in temperature results in increasing hydrophilicity of anionic surfactants but nonionic surfactants have the opposite trend. The studied extended surfactant has the polypropylene oxide groups inserted between the hydrophobic tail and hydrophilic head group, making it less sensitive to temperature than conventional anionic surfactants [39]. This may suggest that the studied extended surfactant has mixed properties between anionic and nonionic surfactants, explaining good oily detergency over a wide range of washing temperatures.

Figure 4.5(c-2) shows the oil redeposition as a function of washing temperature for both DI water solution and 0.3 wt% surfactant with 1 wt% NaCl concentrations for both polyester and cotton fabrics. For DI water, the oil redeposition reached the maximum at about the melting point for both studied fabrics. For the surfactant solution, the oil redeposition on the cotton fabric reached a slight minimum at the melting point whereas the oil redeposition on the polyester fabric showed a sharp decrease with increasing temperature at the melting point, similar to the decrease in oil removal at the melting point. For cotton, this anomalous behavior is not seen. As shown in Figures 4.5(b-2) and 4.5(a-2), 0.3 wt% surfactant with 1 wt% NaCl concentration and 0.1 wt% surfactant and 5 wt% NaCl concentration, the oil redeposition generally decreased with increasing temperature just as oil removal generally increased with temperature. So the surprising temperature inversion observed at the melting point, observed only for polyester, is evidenced in both oil removal and oil redeposition.

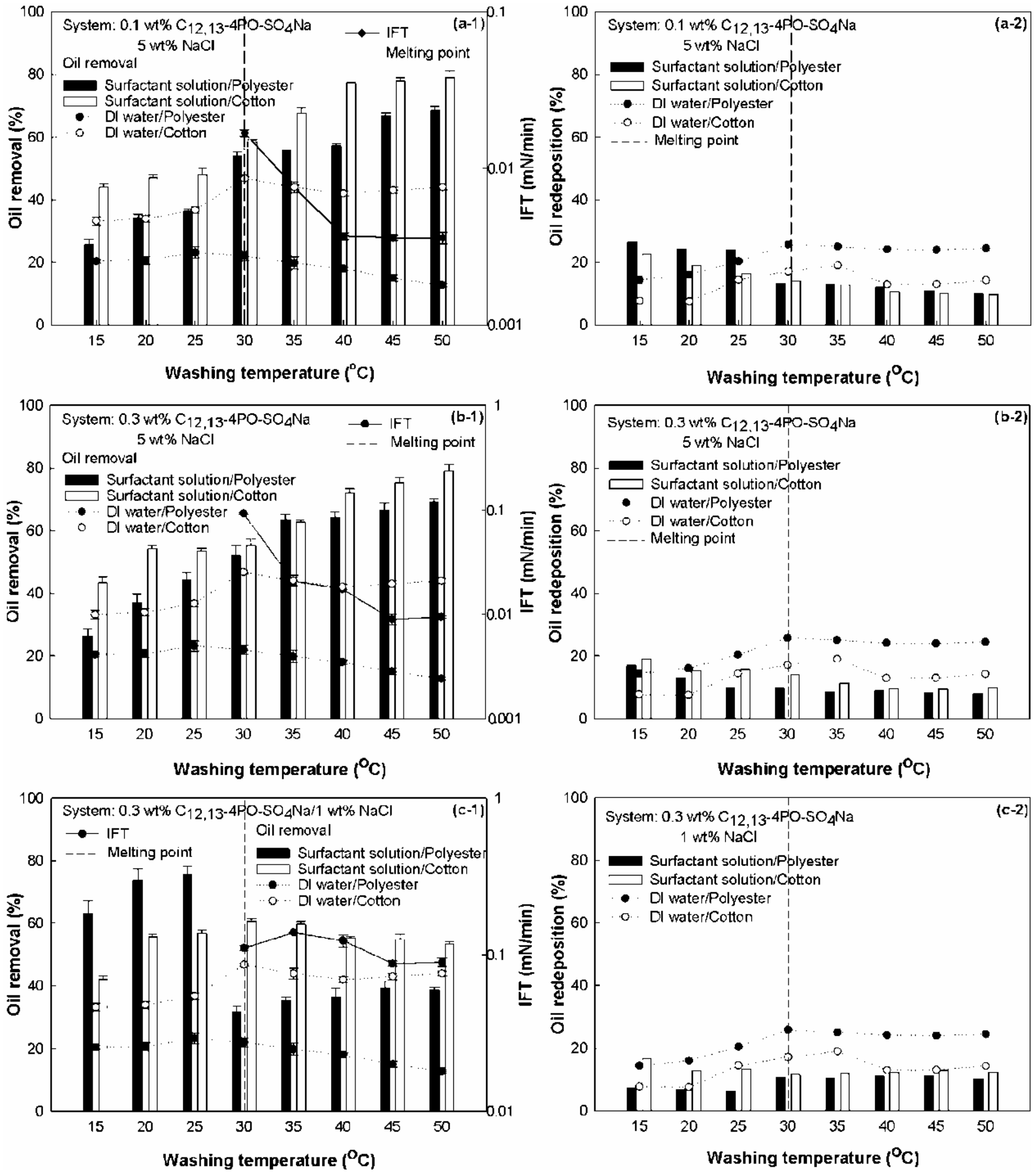


Figure 4.5 Oil removal and redeposition as a function of washing temperature in relation to equilibrium IFT at (a) 0.1 wt%$C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl, (b) 0.3 wt%$C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl, and (c) 0.3 wt%$C_{12,13}(PO)_4SO_4Na$ with 1 wt% NaCl on both test fabrics of cotton and polyester.

Table 4.2 The effect of soiling procedure on detergency performance for polyester

Washing Temperature (°C)	Oil removal (%)	
	Not heated soiling (25 °C)	Heated soiling (40 °C)
15	63.13±4.12	30.96±2.84
20	73.79±3.69	35.23±1.91
25	75.50±2.80	30.05±3.88
30	31.63±1.84	40.90±3.91
35	35.32±1.24	50.95±1.73
40	36.40±3.02	46.74±2.08

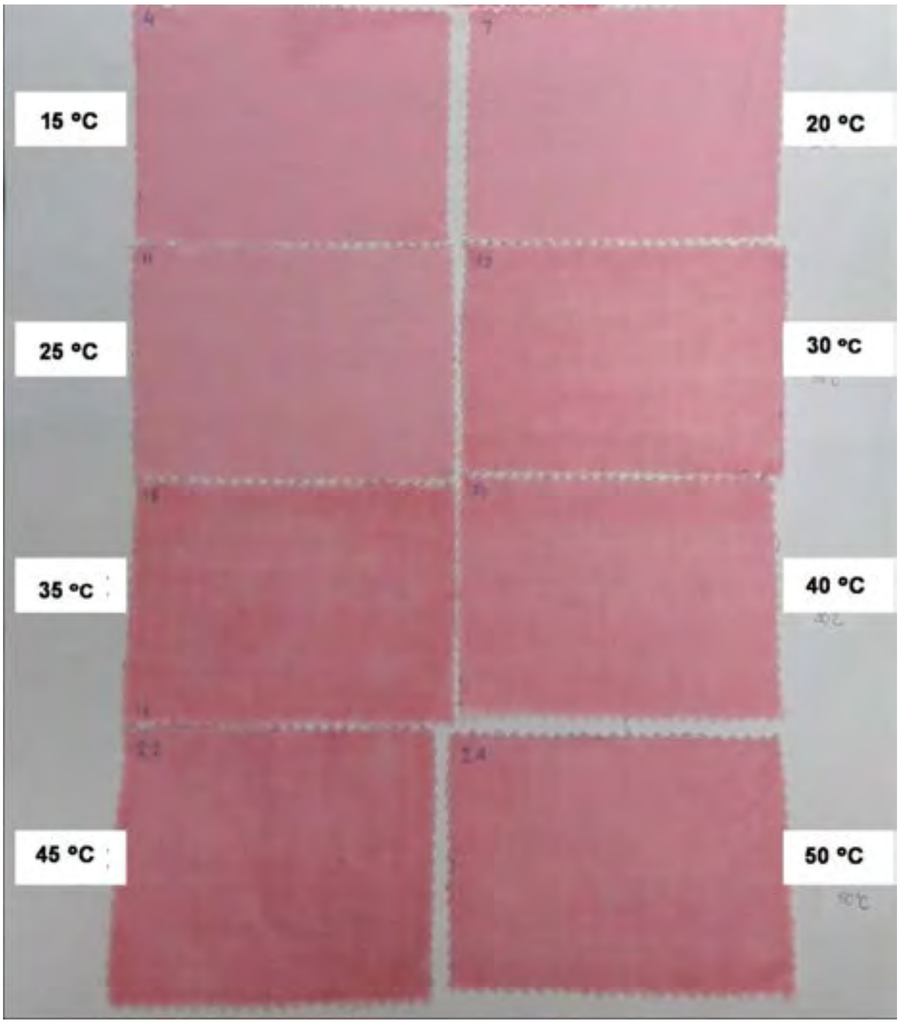


Figure 4.6 Picture of washed fabrics at different washing temperatures of 0.3 wt%$C_{12,13}$-4PO-SO_3Na with 1 wt% NaCl.

4.4.6 Solubilization Results

Figure 4.7 shows both solubilized and unsolubilized portions of removed oil in different washing solutions at different washing temperatures for both test fabrics at 20 min. For any washing temperature, most of removed oil was found to be in a separate dispersed phase (either emulsified liquid droplets or dispersed solid particles) with a very small portion solubilizing in micelles. The solubilized portion slightly increased with increasing washing temperature. An increase in surfactant concentration from 0.1 to 0.3 wt% increased the solubilization portion of removed oil. This is because an increase in surfactant concentration simply increases the concentration of micelles, leading to an increase in oil solubilization. The results of most removed oil being in free oil particles suggest that the dispersion stability of detached oil particles plays an important role in the overall detergency performance. The differences between the oil solubilization at 20 min and the equilibrium oil solubilization at different temperatures are shown in Table 4.3. For all studied systems, equilibrium oil solubilization was attained at a very long time (about 24 h). Most of the oil solubilization values at 20 min were around 10% of the equilibrium oil solubilization values, suggesting that the washing time used in the washing experiment as well as in actual application is too short for effective solubilization so most detached oil is in unsolubilized form. Comparing the three surfactant systems in term of g of oil /g of surfactant in Fig.4.8 shows that at any temperature below the melting point (~30 ºC) for all studied surfactant systems, the equilibrium oil solubilization values were almost unchanged with temperature and significantly lower than those at any temperature higher than the melting point. With increasing washing temperature above the melting point, the equilibrium oil solubilization value considerably increased and tended to level off at a temperature around 40 - 50 ºC.

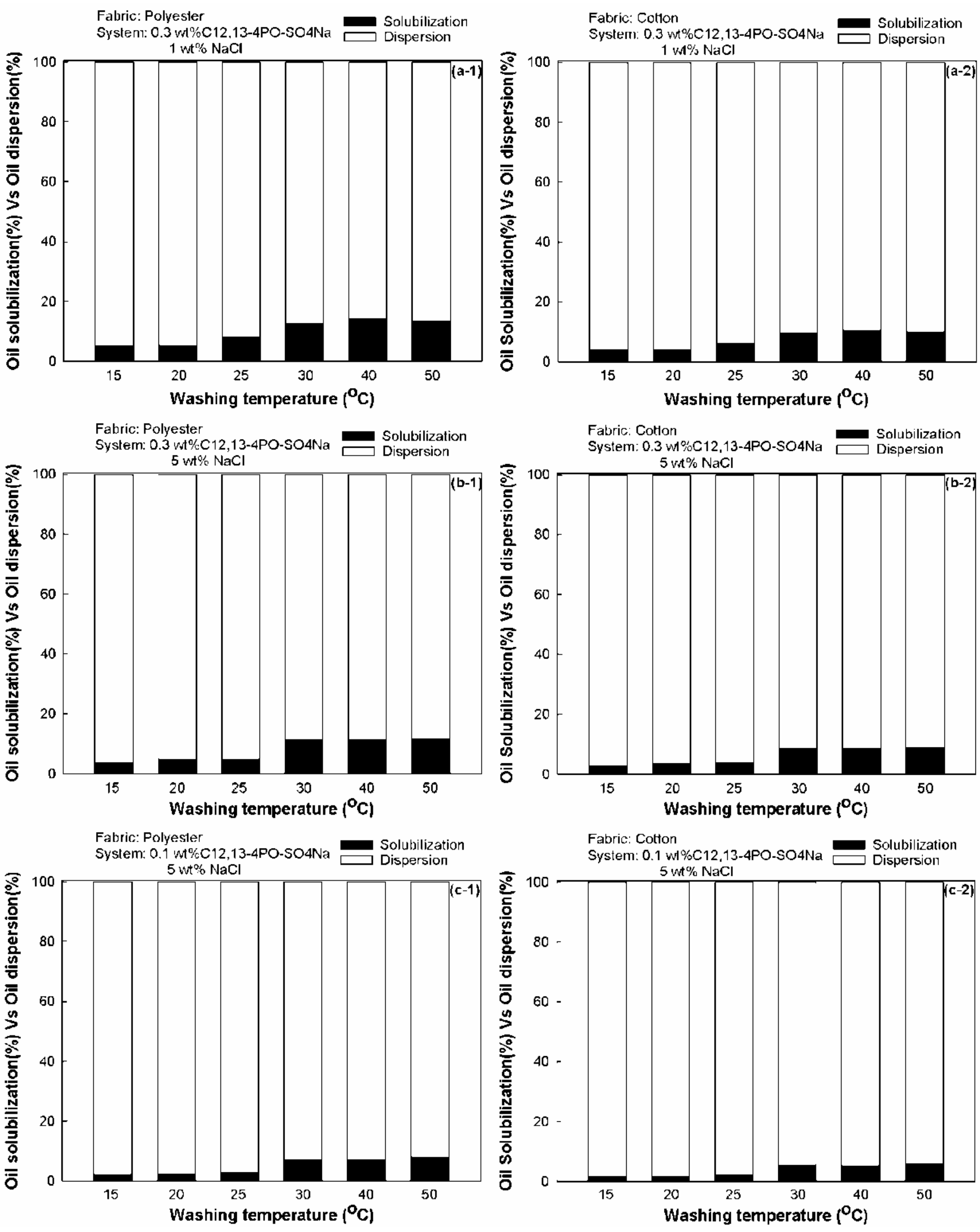


Figure 4.7 Solubilized portions and unsolubilized portions of removed oil at 20 min; (a) 0.3 wt%$C_{12,13}(PO)_4SO_4Na$ with 1 wt% NaCl, (b) 0.3 wt%$C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl, and (c) 0.1 wt%$C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl on both test fabrics of cotton and polyester.

Table 4.3 The ratio of oil solubilization at 20 min to equilibrium oil solubilization at different surfactant systems

0.3 wt%C12,13-4PO-SO4Na/1wt% NaCl			
Temperature	Oil solubilization (g/L)		Ratio
(°C)	At 20 min	At equilibrium	(At 20min/At equilibrium)
20	0.0235±0.0035	0.190±0.020	0.1236
25	0.0365±0.0034	0.342±0.012	0.1069
30	0.0570±0.0014	0.226±0.016	0.2519
40	0.0635±0.0233	0.662±0.030	0.0959
50	0.0605±0.0149	0.634±0.033	0.0955
0.3 wt%C12,13-4PO-SO4Na/5wt% NaCl			
Temperature	Oil solubilization (g/L)		Ratio
(°C)	At 20 min	At equilibrium	(At 20min/At equilibrium)
20	0.0210±0.0014	0.304±0.023	0.0691
25	0.0220±0.0056	0.262±0.005	0.0841
30	0.0510±0.0010	0.272±0.004	0.1872
40	0.0520±0.0014	0.506±0.006	0.1028
50	0.0500±0.0028	0.532±0.038	0.0940
0.1 wt%C12,13-4PO-SO4Na/5wt% NaCl			
Temperature	Oil solubilization (g/L)		Ratio
(°C)	At 20 min	At equilibrium	(At 20min/At equilibrium)
20	0.0105±0.0021	0.109±0.008	0.0959
25	0.0125±0.0035	0.104±0.026	0.1202
30	0.0318±0.0017	0.123±0.008	0.2585
40	0.0312±0.0024	0.160±0.009	0.1950
50	0.0350±0.0036	0.233±0.012	0.1502

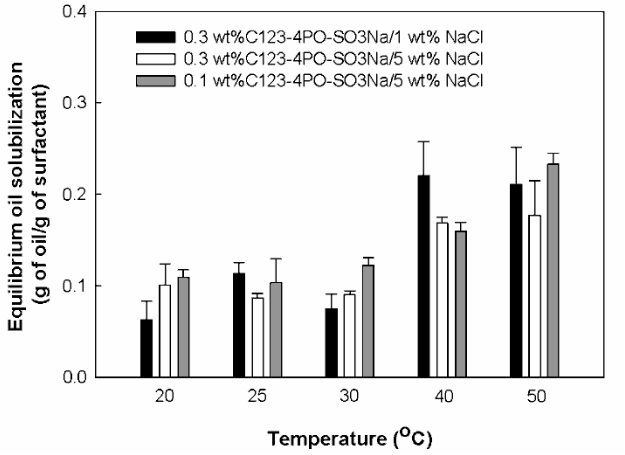


Figure 4.8 Equilibrium oil solubilization in different surfactant systems as a function of temperature.

4.4.7 Particle Size Distribution of Detached Oil Particles after Wash Step

Table 4.4 shows the particle size distribution of methyl palmitate particles suspended in the washing solution after the 20 min wash step for both fabrics using either surfactant or DI water at 25 ºC. At 25 ºC, the solid nature of the particles of methyl palmitate made it possible to measure the particle size distribution. For any wash system, the particle size distribution of the methyl palmitate solid particles detached from any fabric consisted of a trimodal distribution or three ranges of particle sizes (1–5, 5-100, 100-600 µm). Compared to the surfactant formulation, when DI water was used in the wash step, the detached particles of methyl palmitate had larger sizes in the ranges of 5–100 and 100–600 µm with mean sizes of about 100 and 120 µm for the cotton and polyester fabrics, respectively. Interestingly, the use of surfactant resulted in particle sizes of the detached methyl palmitate solid particles being about one third to one fourth of those of the DI water system. The results suggest that surfactant solution penetrates the methyl palmitate by wetting, the soil is then dislodged as small particles or droplets, so the small particle size correlates with good wettability leading to high detergency efficiency.

Table 4.4 Particle size distribution and averaged sizes of methyl palmitate after washing step with DI water and surfactant solution with various salinities at 25 °C

Washing solution	Cotton						
	1–5 µm		5–100 µm		100–600 µm		Mean size
	Size	Vol.	Size	Vol.	Size	Vol.	
	(µm)	(%)	(µm)	(%)	(µm)	(%)	(µm)
De-ionized water	2.32±0.02	9.5	23.2±1.11	58	282±5.28	32	101±3.88
$C_{12,13}(PO)_4SO_4Na$	2.46±0.01	31	10.6±0.13	61	309±1.84	8.2	36.2±1.78
$C_{12,13}(PO)_4SO_4Na$/ 1wt%NaCl	2.39±0.05	21	15.6±0.51	71	276±9.31	8	29.4±2.47
$C_{12,13}(PO)_4SO_4Na$/ 3wt%NaCl	2.43±0.11	21	14.3±0.77	74	223±3.48	4.5	21.0±0.67
$C_{12,13}(PO)_4SO_4Na$/ 5wt%NaCl	2.40±0.04	33	12.6±1.98	62	289±10.2	5.5	24.1±3.46
$C_{12,13}(PO)_4SO_4Na$/ 7wt%NaCl	2.37±0.01	35	13.6±0.04	60	348±2.66	5.3	24.7±2.62
Washing solution	Polyester						
	1–5 µm		5–100 µm		100–600 µm		Mean size
	Size	Vol.	Size	Vol.	Size	Vol.	
	(µm)	(%)	(µm)	(%)	(µm)	(%)	(µm)
De-ionized water	2.76±0.48	6.50	30.0±0.11	57.1	280±26.8	36.4	120±17.8
$C_{12,13}(PO)_4SO_4Na$	2.51±0.01	24	11.8±0.06	64.1	313±12.2	11.7	45.8±1.41
$C_{12,13}(PO)_4SO_4Na$/ 1wt%NaCl	2.37±0.01	28	13.3±0.35	62.1	313±8.07	9.79	40.0±0.55
$C_{12,13}(PO)_4SO_4Na$/ 3wt%NaCl	2.39±0.01	26	13.1±0.17	63.6	344±4.67	10.0	44.4±1.73
$C_{12,13}(PO)_4SO_4Na$/ 5wt%NaCl	2.37±0.01	24	14.3±0.51	66.7	335±3.25	8.81	38.7±1.81
$C_{12,13}(PO)_4SO_4Na$/ 7wt%NaCl	2.38±0.11	20.2	15.8±3.51	71.3	289±25.9	8.50	37.2±6.68

4.4.8 Point of Zero Charge and Zeta Potential Results

Table 4.5 shows the point of zero charge (PZC) and zeta potential values of methyl palmitate, cotton, and polyester particles in various solution systems at 25 °C (pH 4 – 6). The PZC values of methyl palmitate, cotton, and polyester were 2.20, 2.90, and 2.40, respectively, indicating that the net surface charges of these three materials are always negative in detergency experiments because of the much higher pH values of both DI water and the studied extended surfactant solutions. The magnitude of the zeta potential of methyl palmitate is high despite it being fairly hydrophobic (contact angle with water of 82 degrees) because of the ester functional group in methyl palmitate which is hydrolyzed into carboxyl and hydroxyl groups to provide negative charges [14, 15, 40, 41]. When DI water was replaced by the 0.1 wt% surfactant solution, the zeta potential of methyl palmitate became more negative from -46.2 to -157 mV because of the anionic surfactant adsorption. The zeta potential values of both cotton, and polyester in the studied extended surfactant solution became more negative as compared to those in DI water and they also increased when the surfactant concentration increased [42]. This is probably due to higher surfactant adsorption on the solid with higher surfactant concentration, although higher adsorption doesn't necessarily occur since concentrations are well above the CMC. In contrast, with increasing NaCl concentration for any fixed extended surfactant concentration, the zeta potential of methyl palmitate, cotton, and polyester became less negative, due to compression of the double layer or reduction of Debye length next to the surface with increasing ionic strength [43, 44]. A high absolute zeta potential indicates that electrostatic repulsion could be an important factor in dispersion stability [45, 46].

Table 4.5 Point of zero charge (PZC) and zeta potential of methyl palmitate, cotton, and polyester in various solutions at 25 °C

Properties	Cotton	Polyester	Methyl Palmitate
Point of Zero Charge (PZC)	2.90*	2.40*	2.20
Zeta Potential (mV) in;			
DI water	–20.3±5.0	–50.0±5.0	–46.2±2.7
0.1 wt%$C_{12,13}$-4PO-SO_4Na	–73.5±6.7	–139 ±7.6	–157 ±5.5
0.1 wt%$C_{12,13}$-4PO-SO_4Na/1wt% NaCl	–54.9±3.4	–60.9±7.2	–57.0±4.3
0.1 wt%$C_{12,13}$-4PO-SO_4Na/3wt% NaCl	–48.0±4.8	–54.4±4.6	–53.7±2.0
0.1 wt%$C_{12,13}$-4PO-SO_4Na/5wt% NaCl	–33.3±1.0	–33.1±2.8	–34.1±2.3
0.1 wt%$C_{12,13}$-4PO-SO_4Na/7wt% NaCl	–30.8±2.7	–28.7±2.5	–29.9±1.2

*Data from previous work [14]

4.4.9 The Dispersion Stability Results

Figure 4.9 shows the dispersion stability (absorbance) of methyl palmitate solid particles (in terms of average absorbance values) as a function of salinity in the two surfactant systems (0.1 and 0.3 wt%) at 25 ˚C. The higher the absorbance, the greater the concentration of particles dispersed in the aqueous phase and thus the higher the dispersion stability. The presence of extended surfactant without added NaCl only marginally improved the dispersion stability of methyl palmitate solid particles as compared to DI water despite the fact that the zeta potential is much more negative in the presence of surfactant. Increasing NaCl concentration can greatly improve the dispersion stability; the maximum dispersion stability was found in the salinity range of 3 to 5 wt% which also produced the best detergency performance. So, dispersion stability is an important component of detergency since the dominant mechanism of solid removal is as particles, not through solubilization. However, the zeta potential decreases in magnitude with increasing NaCl concentration. Comparing effects of surfactant and NaCl concentrations on zeta potentials and dispersion stability lead to the important conclusion that electrostatic stabilization of the dispersed particles is not the dominant factor in dispersion stability. Dispersion stability is not highest when the zeta potential is at maximum value. Parfitt and Wharton [47] studied the dispersion of solid particles in a surfactant solution and found that the dispersion followed a three-stage process. First, the wettability of solid particle surface occurred, as reflected by the corresponding contact angle. The surfactant solution is better able to penetrate into inter-particle clusters and crevices due to the reduction of the contact angle. Second, the solid particles are suspended in the solution by wetting, and thus dispersion stability occurs. Therefore, deaggregation of the solid particle is required to achieve a good dispersion by repulsive force between charged particles. After the solid particles have been dispersed in the solution, the danger is that they will coagulate (aggregate) and redeposit. Therefore, the wettability (contact angle), particle size distribution, and dispersion stability of the particles are important to detergency efficiency.

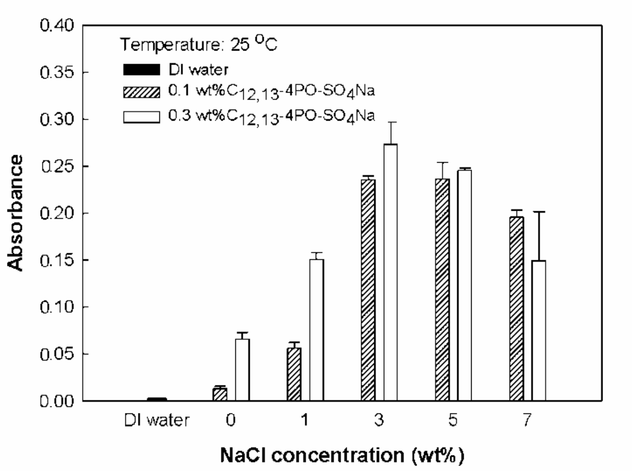


Figure 4.9 Dispersion stability (absorbance) of methyl palmitate particles in surfactant solutions as a function of salinity as compared to DI water at 25 °C.

4.4.10 Visual Observations

Figure 4.10 shows pictures of the washing solutions after the wash step using DI water (Figure 10a) and two surfactant solutions (0.1 wt% surfactant with 5 wt% NaCl and 0.3 wt% surfactant with 1 wt% NaCl) at temperatures below and above the oil's melting point. In DI water, the removed oil was found mostly in solid particles floating on the surface of washing solution with relatively large particle sizes at 25 °C and much larger liquid droplets at 35 °C. For detergency with surfactant solutions, the removed oil was found to suspend in the washing solution with much smaller particles and without either solid or liquid methyl palmitate particles or droplets floating on the surface.

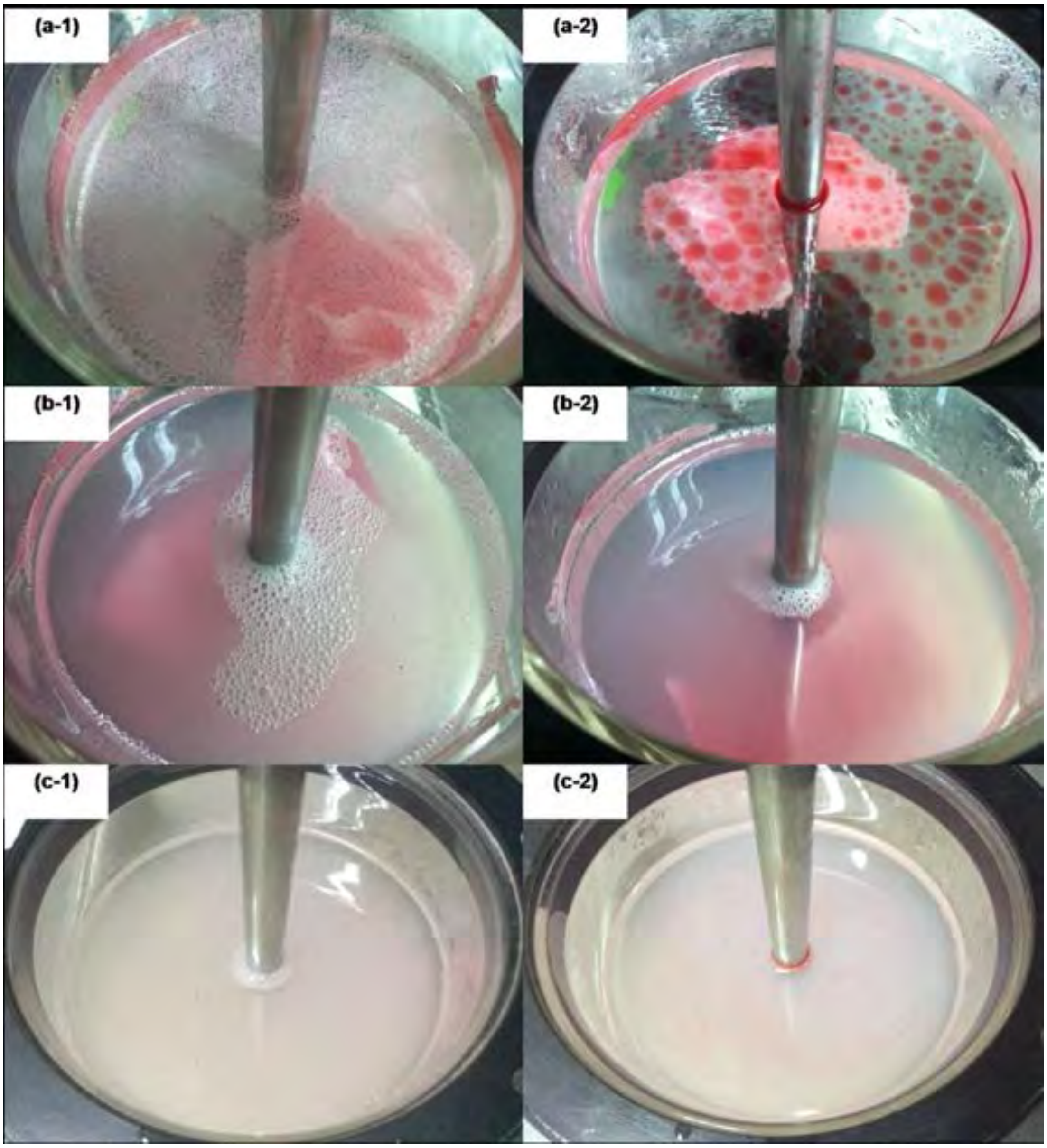


Fig. 4.10 Photographs of washing solutions after the wash step: (a-1) at below the melting point (25 °C) in DI water, (a-2) above the melting point (35 °C) in DI water, (b-1) below the melting point in 0.1 wt%$C_{12,13}(PO)_4SO_4Na$ and 5 wt% NaCl, (b-2) above the melting point in 0.1 wt%$C_{12,13}(PO)_4SO_4Na$ and 5 wt% NaCl, (c-1) below the melting point in 0.3 wt%$C_{12,13}(PO)_4SO_4Na$ and 1 wt% NaCl, (c-2) above the melting point in 0.3 wt%$C_{12,13}(PO)_4SO_4Na$ and 1 wt% NaCl.

4.4.11 Mechanistic Insights

Results on this paper shows the relationships between the removal mechanism of solid fat soil below and above the soil melting point. Above the melting point, lower IFT results in better detergency with varying temperature or salinity. Therefore, roll-up of liquid soil is an important mechanism [6-13]. Below the melting point, the detachment of soil as solid particles occurs by surfactant prenetration, leading to the soil breaking up and floating away from the fabric surface into solution as small particles [48-50]. Surfactant and salinity improves wetting, dispersion stability, and decreases detached particle size. Unlike particulate soil, electrostatics are not the primary driving force for detergency.

4.5 Acknowleadgements

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CHAPTER V

LAUNDRY DETERGENCY OF SOLID NON-PARTICULATE SOIL OR WAXY SOLIDS: PART II. EFFECT OF SURFACTANT TYPE

5.1 Abstract

Solid monoglyceride or solid fat detergency is a particular interest especially at a washing temperature below its melting point. In this work, methyl palmitate or palmitic acid methyl ester, having a melting point around 30 °C, was used as a model of solid non-particulate soil or waxy soil being removed from either hydrophilic surface (cotton fabric) or hydrophobic (polyester) surface by using different surfactants: alcohol ethoxylate (EO9), sodium dodecyl sulfate (SDS), methyl ester sulfonate (MES), methyl ester ethoxylate (MEE), and two extended surfactants ($C_{12,14}$-10PO-2EO-SO_4Na and $C_{12,14}$-16PO-2EO-SO_4Na). The effects of surfactant type and concentration, salinity, washing temperature, and soiling procedure on detergency performance and oil redeposition were investigated. The results show that the detergency efficiency at a 0.2 wt% surfactant concentration and 5 wt% NaCl concentration gradually increased with increasing washing temperature in most studied surfactant solutions whereas the oil redeposition exhibited an opposite trend to the oil removal for both above and below the melting point of methyl palmitate on both studied fabrics. The detergency performance of methyl palmitate to be soiled with heating was significantly lower than that of methyl palmitate to be soiled without heating especially for a washing temperature lower than the melting point since the methyl palmitate could penetrate into the fabric matrix well by heating. The nonionic surfactant (EO9) showed the highest detergency efficiency in the range of 73 to 94 % at any washing temperature especially on the polyester fabric. When a washing temperature was below the melting point, detergency performance was found to correlate well with the contact angle of surfactant solution on the methyl palmitate surface for all studied surfactants. The results suggest that the removal of liquefied methyl palmitate oil results from both roll up and solubilization while that of the solidified methyl palmitate is governed by the detachment ability by mechanical force, surfactant adsorption causing a lower contact angle, and dispersion stability of detached solidified oil particles. Most of detached oil in both liquefied and solidified particles are in unsolubilized forms.

Keywords Waxy solids, Solid fat soil, Methyl palmitate, Alcohol enthoxylate, Laundry detergency

5.2 Introduction

The washing of clothes is a part of our everyday routine. Around 80 – 90 % of energy consumption by a washing machine is used to heat water. Therefore, a use of low temperature washing can save up to 70 % of the electricity cost [1]. However, cold temperature washing has poorer efficiency than that at a higher washing temperature. Bubl [2] and Morris [3] studied the effect of washing temperature on the removal of synthesized sebum from cotton fabric using two different detergents (regular and cold-water detergents) and they found that both detergents worked better at a higher washing temperature. Fort et al. [4] studied the removal of fatty soils and particulate soils from three different polymer substrates (cellulose, nylon, and polyethylene) by using different surfactant types at both low (20 °C) and high (60 °C) washing temperatures. The rate of soil removal increased when the degree of hydrophilicity of the substrate increased and it was much faster at a higher washing temperature. Moreover, sodium lauryl sulfate (anionic surfactant) was the best candidate for fatty soil removal from the cellulose whereas nonylphenyl polyethylene glycol (nonionic surfactant) was the best for the polyethylene terephthalate (hydrophobic surface). Morris and Prato [5] found that the removal of both particulate and oily soils from cotton fabric increased with an increase in washing temperature whereas for a nonpolar oily soil on polyester surface, the removal increased with decreasing washing temperature. Illman et al. [6] and Spangler et al. [7] found the similar results that the removal of sebum from Dacron, nylon, or polyester in cold water was higher than that by using hot water and the improvement of detergency performance was increased under the presence of nonionic surfactant.

Solid non-particulate soils or solid fat soils are fats that mostly become solid at room temperature (25 °C); e.g., butter, margarine, tallow, lard, or solidified hamburgers or bacon grease. There are not many researchers to explore the mechanisms of low temperature laundry detergency of solid non-particulate soil. Scheuing [8] studied the detergency mechanisms of tristearin (model solid fat soil) by using Fourier transform infrared spectroscopy (FT-IR) and reported that the removal of solid triglycerides from solid surface was more complex than that of solid hydrocarbon soils because of the polymorphism in the crystal structure of tristearin. Powe [9] studied the removal of motor oil, mineral oil, petrolatum, and paraffin from cotton and reported that the removal of any studied soil increased with increasing washing temperature and the maximum soil removal was found somewhere near their melting points. Scott [10] also found similar results that for octadecane (hydrocarbon) and tripalmitin (triglyceride), the removal markedly increased with increasing washing temperature above their melting points. Kawase et al. [11, 12] found that the dominant mechanism to remove myristic acid (solid fatty acid soil) at a low washing temperature was solubilization by using both nonionic and anionic surfactants which were alcohol ethoxylate and sodium dodecyl sulfate, respectively.

Our research group has studied the oily soil removal mechanisms using different liquid oils and surfactant systems and found good correlation between interfacial tension (IFT) and oil removal [13-19]. Recently, our previous work published the mechanism and performance of methyl plamitate as a model of solid non-particulate soil (waxy solid) from fabrics by using an extended surfactant at both below and above the soil's melting point (~30 °C). The removal of solid non-particulate soil was found to be mostly unsolubilized form with a small fraction of micellar surfactant solubilization on both below and above the soil's melting point. As a result, the detachment of solid non-particulate soil was small particles and dispersed in wash solution [20].

Alcohol ethoxylates (EO), nonionic surfactants are widely used because of many desirable characteristics such as low to moderate foaming ability, low critical micelle concentrations, high water hardness tolerance, and high solubilization capacity for oily soils, mildness to human skin, and good biodegradability. Hama et al. [21] reported that ethoxylated methyl laurate with 60 to 70 % EO content was found to be the most suitable candidate for household detergents. Raney and Benson [22] reported that the maximum hydrocarbon soil removal was found above the surfactant cloud point at the phase inversion temperature (PIT) and alcohol ethoxylates with 4 to 5 EO groups were good for nonpolar soil removal while alcohol ethoxylates with 6 to 9 EO groups were very effective for sebum soil removal. Goel [23-25] also studied the oily soil removal from fabric by using alcohol ethoxylates. The maximum detergency efficiency increased with increases in both the average EO moles in nonionic surfactant and the ratio of nonionic to anionic surfactant concentrations at a certain electrolyte level. The optimum EO moles in alcohol ethoxylates increased as the electrolyte concentration in the system increased. Moreover, the oil/water interfacial tension (IFT) showed an opposite trend to the detergency results. The lower the IFT, the higher the detergency performance. Sodium dodecyl sulfate (SDS) is one of the most well-known and widely used surfactants for research works and it was also selected in this study. Methyl ester sulfonate (MES) and methyl ester ethoxylate (MEE) are a derivative of methyl ester (ME) which is obtained from natural fats and oils, renewable resources such as coconut oil and palm oil. Due to environmental concerns and the limitation of petroleum and petrochemicals, MES and MEE are expected to replace linear alkyl benzene sulfonate (LAS) and alcohol ethoxylates (EO) respectively, which are the main components in most commercial detergent products. MES and MEE are cost competitive with petroleum-based surfactants and they are more environmentally friendly and considered as a renewable resource. Further, MES and MEE have shown preferable properties compared to LAS and alcohol ethoxylates respectively [26-32]. Hence, these two surfactants were chosen in this research work.

An extended surfactant has a group of intermediate polarity, such as polypropylene oxide (PO) or polypropylene-polyethylene oxide (PO-EO) group, inserted between the hydrophilic head and hydrocarbon tail group. It can extend further into both oil and aqueous phases, resulting in a smoother transition between the hydrophobic and hydrophilic regions at the interface. Phan et al. [33] reported that more than 80 % of canola oil removal was achieved by using a single extended surfactant ($C_{14,15}$-8PO-SO_4Na) at concentrations as low as 125 ppm at a low temperature of 25 oC. Do et al. [34] reported that the mixture of a linear extended surfactant (C_{10-18}PO-2EO-SO_4Na) and a hydrophobic twin-tailed sodium dioctylsulfosuccinate surfactant showed synergism in a Winsor type III microemulsion formulation, leading to high detergency performance of vegetable oils and semi-solid fats at low salinity and washing temperature below the oil's melting point.

In this paper, methyl palmitate or palmitic acid methyl ester, a monoglyceride with a melting point around 30 °C, was used as a model solid fat or oily soil being removed from either hydrophilic surface (cotton fabric) or hydrophobic surface (polyester fabric) by using different surfactants including alcohol ethoxylate (EO9) with a C12 to C14 alkyl chain length and 9 ethylene oxide groups, sodium dodecyl sulfate (SDS) with a C12 alkyl chain length, methyl ester sulfonate (MES) with a C14 alkyl chain length, methyl ester ethoxylate (MEE) with a C12 alkyl chain length and 18 ethylene oxide groups, and two extended surfactants ($C_{12,14}$-10PO-2EO-SO_4Na and $C_{12,14}$-16PO-2EO-SO_4Na) with 12 to 14 carbons in their hydrophobic tails, 10 and 16 propylene oxide and 2 ethylene oxide groups. For detergency performance experiments above the melting point, IFT was measured in order to confirm the correlation between the IFT value and the percentage of oil removal. For washing experiments below the melting point, several important parameters including zeta potential of oil particles and fabrics, oil dispersion stability, contact angles of different surfactant solutions on methyl palmitate, particle sizes of detached methyl palmitate, and oil solubilization after the wash step were measured and used to explain the mechanisms of solid non-particulate soil detergency.

5.3 Experimental Procedures

5.3.1 Materials

Methyl palmitate or palmitic acid methyl ester (99.8% purity) and Oil red O (solvent Red 27, No. 26125) were purchased from Sigma-Aldrich (BKK, Thailand). Two studied fabrics; pure cotton and pure polyester were purchased from Test fabrics, Inc. (Middlesex, NJ, USA). Alcohol ethoxylate (EO9) with a C12 to C14 alkyl chain length and 9 ethylene oxide groups with an active content of 99.9

wt% was kindly supplied by Thai Ethoxylate Company Limited, BKK, Thailand. Methyl ester ethoxylate (MEE) with a C12 alkyl chain length and 18 ethylene oxide groups with an active content of 90.2 wt% and methyl ester sulfonate (MES) with a C14 alkyl chain length with an active content of 99.8 wt% were kindly prepared by Lion Corporation, Tokyo, Japan. Sodium dodecyl sulfate (SDS) with an active content of 99 wt% was purchased from Sigma-Aldrich, BKK, Thailand. Two extended surfactants, sodium linear-alkyl polypropoxylated polyethoxylated sulfate (R-(PO)y-(EO)z-SO4Na) with 12 to 14 carbons in their hydrophobic tails, 10 and 16 propylene oxide and 2 ethylene oxide groups with an active content of 24.2 and 23.3 wt%, respectively were donated by Huntsman Petrochemical Corp, Houston, TX. Table 5.1 summaries the properties of all surfactants used in this study. Commercial detergent (Breeze® excel liquid detergent) of a leading brand was purchased from local market and used for comparison purposes. Sodium chloride (NaCl), dichloromethane, and isopropanol, which are all in analytical grade, were purchased from LabScan Asia Co.,Ltd. Deionized water was used to prepare all solutions.

Table 5.1 Surfactant properties

Surfactants	Formula	Type	%Active	MW	CMC
				(g/mol)	(mM)
Alcohol ethoxylate (EO9)	$C_{12,14}$-$(OCH_2CH_2)_9OH$	nonionic	99.9	596	0.075
Methyl ester ethoxylate (MEE)	$C_{12}H_{25}COO(EO)_{18}CH_3$	nonionic	90.2	1020	0.22
Sodium dodecyl sulfate (SDS)	$C_{12}H_{25}OSO_3Na$	anionic	99	288	8.1
Methyl ester sulfonate (MES)	$C_{14}H_{25}CH(SO_3Na)COOCH_3$	anionic	99.8	372	1.9
Alkyl-propoxylate-ethoxylate-sulfate (10PO)	$C_{12,14}$-$(PO)_{10}$-$(EO)_2$-SO_4Na	anionic-extended	24.2	970	0.43
Alkyl-propoxylate-ethoxylate-sulfate (16PO)	$C_{12,14}$-$(PO)_{16}$-$(EO)_2$-SO_4Na	anionic-extended	23.3	1318	0.022

5.3.2 Fabric Pretreatment and Soiling Procedure

The studied fabrics of cotton and polyester were cut into 3 x 4 inch swatches and then pre-washed to eliminate all residues of mill-finishing agents by using de-ionized (DI) water for 10 min. The pre-washing method was followed the ASTM standard guide D4265-98 [35]. Approximately 0.1 g of the oil-soluble dye was added to 100 mL of the oil (methyl palmitate) above its melting point. Next, 10 mL of the clear liquid dyed oil was diluted with dichloromethane to 100 mL [36]. The swatches were folded and completely submerged in the diluted dyed oil solution for 5 min at room temperature (25 °C). The soiled fabrics were then unfolded and laid on a flat plate at room temperature overnight in order to dry the soiled swatches. For the soiling with liquefied oil, the diluted dyed oil solution with swatches was left at 40 °C for 2 h and so the soil was liquefied. As a result, the oil could imbibe into the fabric fibers, and it was then left at room temperature (25C) over night before doing detergency experiments. All swatches were freshly soiled for each batch of detergency experiments. By these two soiling methods, the average weight ratios of oil-to-fabric were approximately 0.20±0.01:1 for the cotton and 0.15±0.01:1 for the polyester.

5.3.3 Detergency Experiments and Measurement Methods

The similar procedures used for the detergency experiments and all measurements in this study were described in our previous work [20].

5.4 Results and Discussion

5.4.1 Detergency Performance: Effect of Surfactant Concentration

Figure 5.1 shows the oil removal and oil redeposition as a function of surfactant concentration without salinity addition on two studied fabrics using different surfactant types at 20 ºC in which the methyl palmitate is in solid state. As shown in Fig. 5.1(a-1) and (b-1), for any given surfactant system, the oil removal increases with increasing surfactant concentration and reaches a maximum level. The highest oil removal was found to at a certain surfactant concentration, depending on the washing conditions such as the nature of surfactant, fabric, and soil [2, 3, 37-39]. Interestingly, EO9 gave the most superior detergency performance as compared to all other surfactant systems, especially on the polyester fabric with the highest oil removal of 73.5%. For the cotton fabric, EO9 still showed the highest detergency performance as compared to the other surfactant systems with significantly lower efficiency in the range of 53 to 57 % and at the higher range of surfactant concentration. As shown in Fig. 5.1(a-2) and (b-2), for all studied surfactants, the oil redeposition decreases with increasing surfactant concentration and levels off at a surfactant concentration greater than 0.2 wt% on both fabrics. An increase in surfactant concentration promotes the detachment of oil and also increases the surfactant adsorption onto the detached oil particles, leading to the reduction of oil redeposition. The use of EO9 showed the best oily detergency performance with the lowest oil redeposition as compared to all studied surfactant systems. For further investigation, all studied surfactant systems were fixed at a surfactant concentration of 0.2 wt% to ensure the maximum detergency performance and to rule out the effect of surfactant concentration.

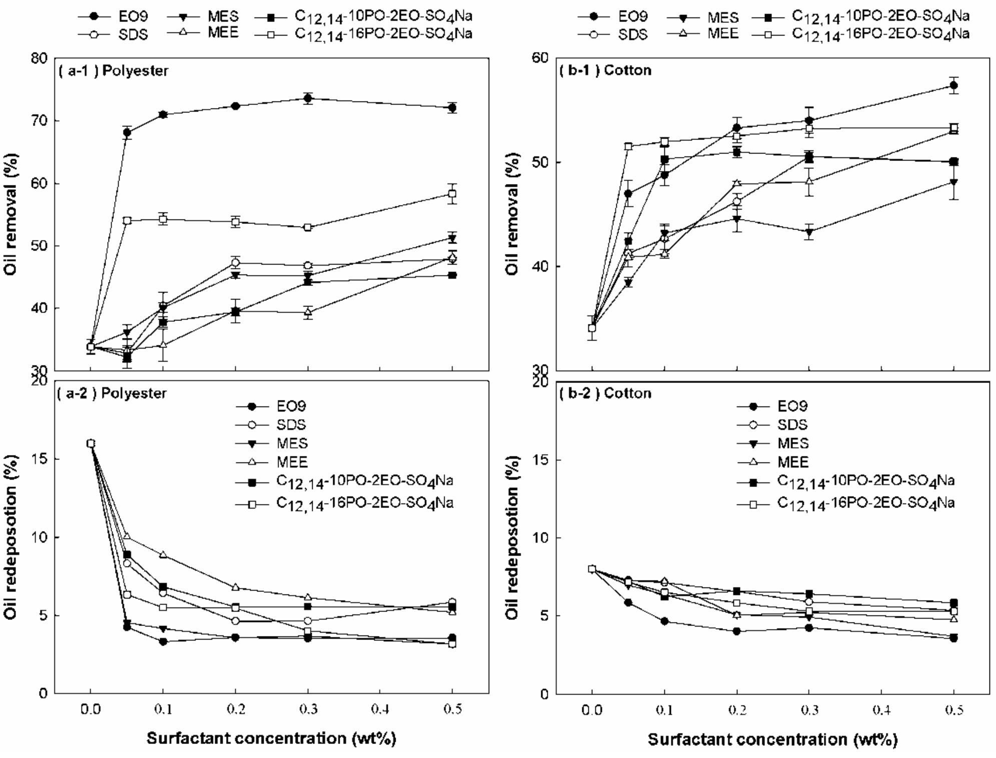

Figure 5.1 Oil removal and redeposition as a function of surfactant concentration at 20 °C on both polyester and cotton fabrics with the soiling temperature of 25 °C.

5.4.2 Detergency Performance: Effect of NaCl Concentration

Salinity has been known to be one of important factors affecting detergency performance, especially for an anionic surfactant system [13-19]. Therefore, the detergency performance of all studied surfactants (except the two extended surfactants due to insufficient quantities for the test) was further evaluated at different NaCl concentrations and a washing temperature of 20 ºC on both studied fabrics. As shown in Figure 5.2, for MES, SDS, and MEE, the detergency performance is significantly affected by NaCl concentration whereas the EO9 detergency (Figure 5.2a) was independent on NaCl concentration [40]. An addition of NaCl in a nonionic surfactant solution has relatively small effects on the surfactant adsorption onto both surfaces of oil and fabric, leading to no significant effect of added NaCl on oil removal. In contrast, an addition NaCl can increase the surfactant adsorption, causing the enhancement of oily soil detergency because of the counter ion effect. Surprisingly, the effect of added NaCl on the MEE system showed a similar trend to those of both MES and SDS since MEE has the polar group of ester in its structure. Interestingly, for the polyester fabric, EO9 gave superior detergency efficiency at any NaCl concentration with efficiency in the range of 72-75 % (Fig. 5.2a) whereas MES gave the maximum oil removal for the cotton fabric with efficiency in the range of 62-65% (Fig. 5.2d). Figure 5.2 also presents the good correlation between contact angle of solution onto methyl palmitate surface and detergency performance of all studied surfactant systems. The contact angle of any studied surfactant system decreased with increasing NaCl concentration and reached a minimum value (best wetting) at 5 wt% NaCl where the detergency performance of all studied surfactants except EO9 was maximum, corresponding to the lowest contact angle. An increase in NaCl concentration attributes to the reduction of repulsive force between the head group of surfactant molecules, leading to an increase in the surfactant adsorption, and resulting in lower contact angle or better wetting of surfactant solution onto solid methyl palmitate surface. As a result, an increase in wettability increases higher penetration of surfactant solution into inter-particle clusters and crevices, leading to better detergency performance. This is the explanation why the EO9 surfactant system having the lowest contact angle onto the studied oil surface provided the highest detergency efficiency, especially for the polyester fabric. However, the detergency efficiency of EO9 did not change with increasing NaCl concentration on both the studied fabrics even though the contact angle value varied with salinity. The use of all studied surfactant systems showed a much higher oil removal and lower contact angles at any given NaCl concentration as compared to the commercial detergent. The good correlation between oily detergency performance and contact angle obtain from the present study is in a good agreement with our previous study [20] and other work [41]. Interestingly, the results showed that it is easier to remove the waxy soil (methyl palmitate) from the polyester fabric than that from the cotton fabric. The hydrogen bonding between hydroxyl groups of cotton and the ether linkages of the hydrophilic groups of EO9 makes the fabric become more hydrophobic, leading to increasing in surface tension between oil and substrate. As a result, the oily soil removal on cotton has lower efficiency than that on polyester when a nonionic surfactant is used [42]. Since most of the studied surfactant systems gave the maximum detergency performance with the lowest contact angle at 5 wt% NaCl, 0.2 wt% surfactant concentration and 5 wt% NaCl concentration were fixed for further investigation.

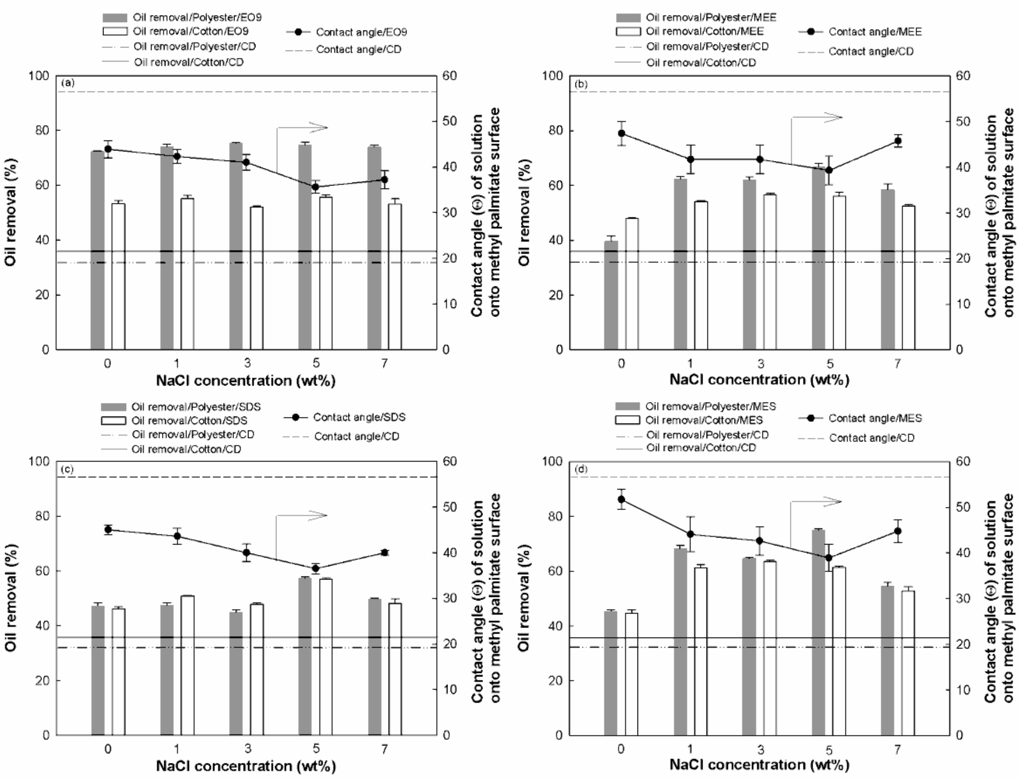

Figure 5.2 Oil removal as a function of NaCl concentration on both polyester and cotton fabrics in relation to the contact angle of solution onto methyl palmitate surface with a surfactant concentration of 0.2 wt%, and at a washing temperature of 20 °C with the soiling temperature of 25 °C: **a** EO9, **b** MEE, **c** SDS, and **d** MES.

5.4.3 Detergency Performance: Effect of Washing Temperature

The washing temperature range of 15 – 50 °C was studied in order to cover both solid and liquid states of methyl palmitate (melting point of 30 °C) for better understanding the mechanisms of solid non-particulate soil removal in relation to oily soil detergency. Figure 5.3 shows the effects of washing temperature on detergency performance and oil redeposition in different surfactant solutions of 0.2 wt% surfactant and 5 wt% NaCl concentrations on both studied fabrics as compared to both commercial detergent and DI water. As shown in Fig. 5.3(a-1) and (b-1), the detergency performance of all studied surfactants is superior to that of either commercial detergent (CD) or DI water on both studied fabrics at any washing temperature. For the cotton fabric and all studied surfactants, the oil removal increased with increasing washing temperature and leveled off when the washing temperature greater than the melting point. An increasing temperature is believed to enhance oil mobility as a result of the reduction of oil viscosity [13, 18]. For the polyester fabric, the detergency performance of all systems gradually increased with increasing washing temperature and reached the maximum at a temperature beyond the melting point except in the DI water system, beyond the melting point, the oil removal slightly decreased with further increasing washing temperature. Interestingly, EO9 showed the highest oil removal at any washing temperature with the efficiency ranges of 74 to 94 % and 60 to 70 % for the polyester and cotton fabrics, respectively. Nonionic surfactants have been widely used for oily soil removal from hydrophobic surfaces such as polyester and nylon whereas anionic surfactants for hydrophilic surfaces in detergency due to the different orientation of the different surfactant types on the different surfaces [4, 7, 42]. Illman et al. [6] found similar results that linear primary alcohol ethoxylate (nonionic surfactant) provided better sebum removal than linear alkylbenzene sulfonate (anionic surfactant) on both low and high washing temperatures because of the solubilization and penetration potential of nonionic surfactant [43].

Figures 5.3 (a-2) and (b-2) show the oil redeposition as a function of washing temperature of all the studied surfactant systems on both polyester and cotton fabrics as compared to the commercial detergent and DI water. For the DI water system, the oil redeposition reached the maximum at a washing temperature about the melting point for both studied fabrics. This trend was not observed when using the commercial detergent or any studied surfactant system. For the commercial detergent, the oil redeposition on the polyester fabric slightly decreased with increasing washing temperature whereas the oil redeposition on the cotton fabric showed sharp decrease and reached a minimum at a washing temperature greater than the melting point. For any studied surfactant system, the oil redeposition slightly decreased and reached the minimum at a washing temperature about the melting point. At a washing temperature below the melting point on the polyester (Fig. 5.3a-2), SDS showed the highest oil redeposition which correlated well with the poorest oil dispersion stability among the studied surfactants, which will be further discussed later.

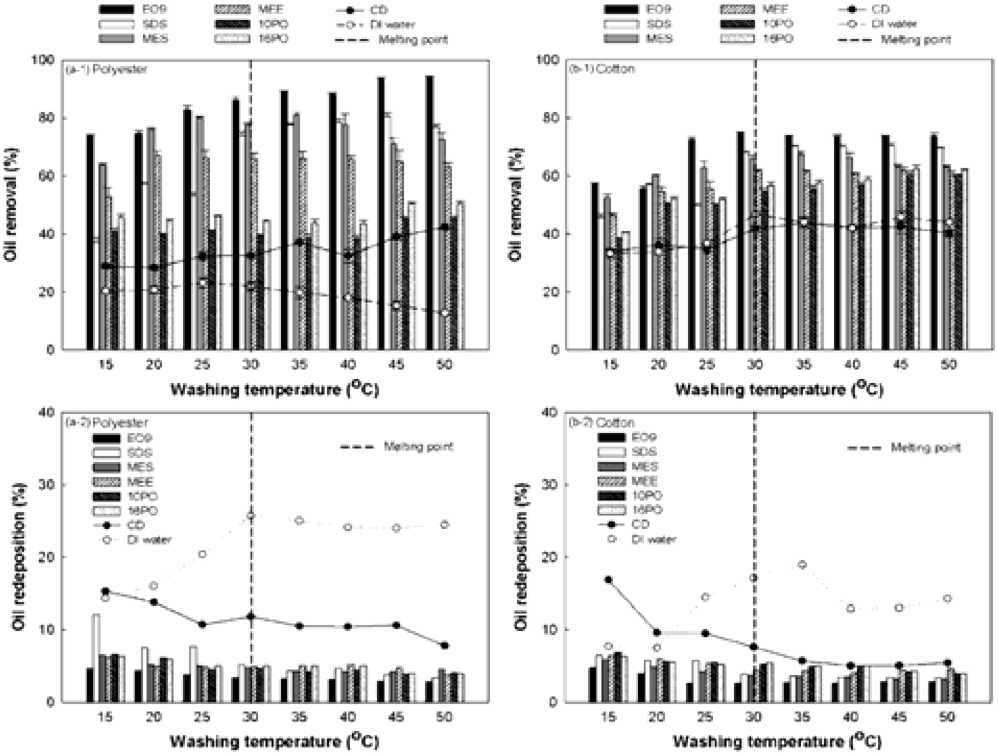

Figure 5.3 Oil removal and redeposition as a function of washing temperature in various surfactant systems at a surfactant concentration of 0.2 wt%, and 5 wt% NaCl on both polyester and cotton fabrics with the soiling temperature of 25 °C.

As shown in Figure 5.4a, for any studied surfactant, the IFT decreased with increasing NaCl concentration and reached a minimum at 5 wt%. Beyond the optimum salinity of 5 wt% NaCl, the IFT of each studied surfactant increased. The effect of salinity on the two anionic surfactants (SDS and MES) was found to be significantly higher than that on the two nonionic surfactants (MEE and EO9) which agree well with literature [44]. MEE had the highest IFT values at any given NaCl concentration. In a comparison between the two nonionic surfactants, EO9 has a lower IFT than MEE at any given NaCl concentration because of the lower critical micelle concentration (CMC) of EO9 than that of MEE, as shown in Table 5.1. Another possible explanation is that the higher ethylene oxide (EO) groups of MEE providing a larger molecular size than that of EO9 lowered the ability to adsorb at the interface resulting in the highest IFT values [45]. Interestingly, for any surfactant system, the maximum oil removal was found at the optimum salinity of 5 wt% NaCl corresponding to the lowest IFT value.

Figure 5.4b shows the IFT value as a function of temperature of any studied surfactant at a surfactant concentration of 0.2 wt% with 5 wt% NaCl, as compared to the commercial detergent. For all studied surfactants, the IFT values with methyl palmitate well below 1.5 mN/m were much lower than those of both DI water (7.9 mN/m) and commercial detergent (2.6 mN/m). The IFT values of most of the studied surfactants were independent on temperature except those of EO9 and MEE. The IFT value of EO9 had different trend as compared to other surfactants in which the IFT value increased from 0.1 to 0.5 mN/m with increasing temperature from 30 to 35 °C. Beyond 35 °C, the IFT value decreased with further increasing temperature. The IFT values of all studied surfactant systems were in the low range of one order of magnitude except SDS giving the lowest IFT values with two order of magnitude at any temperature.

Generally, the maximum detergency efficiency corresponds to minimum oil/water IFT. In comparison between oily detergency efficiency and IFT of all studied surfactants (Figure 5.3 and Figure 5.4b), EO9 gave the highest oil removal at any given washing temperature even though the IFT value was not the lowest. SDS had the lowest IFT with not the highest detergency efficiency at the washing temperature range of 30 to 50 °C. The present results suggest that the oily soil detergency does not rely on the IFT value between the oil and washing solution. In general principle, the lower the IFT value, the higher the oily soil detergency [46]. The present results reveal that the oil redeposition is another important process parameter, affecting oily soil detergency.

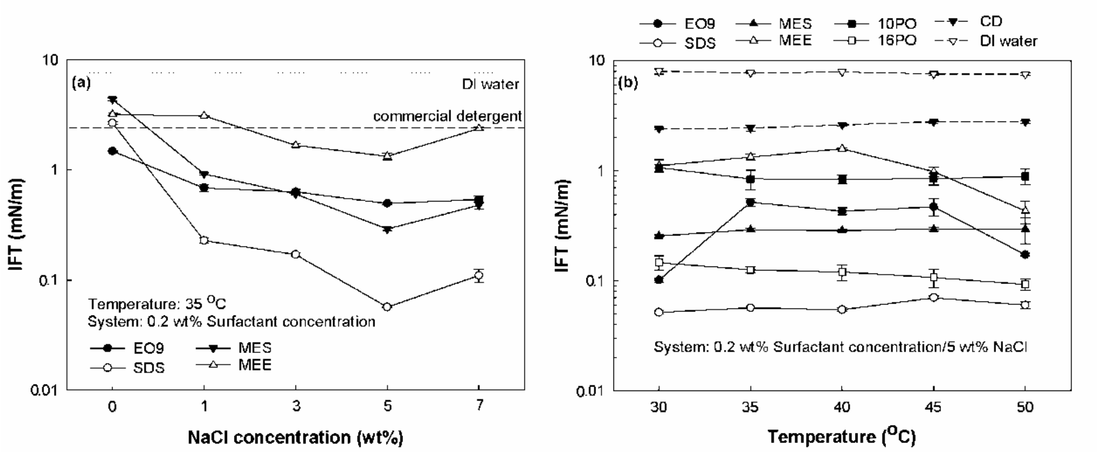

Figure 5.4 The dynamic interfacial tension of methyl palmitate oil and different surfactant solutions having a surfactant concentration of 0.2 wt% as a function of (a) NaCl concentration and (b) temperature.

5.4.4 Solubilization Results

Figures 5.5 and 5.6 show both solubilized and unsolubilized portions of removed oil in different surfactant solutions and washing temperatures at 20 min to represent the wash step for both studied fabrics of cotton and polyester, respectively. The 0.2 wt% surfactant and 5 wt% NaCl concentrations were fixed for the solubilization measurement. For any washing temperature of any studied surfactant, most of removed oil was found to be in free oil either emulsified liquid droplets or dispersed solid particles with a very small solubilized portion in micelles. All surfactant systems, the solubilization portion slightly increased with increasing washing temperature. For anionic surfactants, an increase in temperature moderately increases the extent of polar and nonpolar oil solubilization because an increase in thermal agitation increases the space available for solubilization in micelle [47]. For nonionic surfactants, the effect of temperature significantly show an increase in solubilization as the temperature is raised. The polyoxyethylene chain of the nonionic surfactant loses water hydration as temperature increased leading to increase the critical packing parameter of the surfactant. This causing the transition of the micelle shape to the larger micelles providing more oil solubilization [47]. The solubilization increased rapidly when temperature increases around it's could point

[48]. As a result, EO9 showed the most superior oil solubilization to other surfactants at high temperatures for both studied fabrics. The highest solubilization of EO9 is responsible for the lowest oil redeposition, leading to the highest oil removal as compared to all other surfactants. The equilibrium oil solubilizations at different temperatures of all studied surfactants for methyl palmitate are shown in Fig.5.7. The equilibrium oil solubilization value of any studied surfactant increased with increasing temperature in the studied temperature range. The differences between the oil solubilization at 20 min and the equilibrium oil solubilization at different temperatures are shown in Table 5.2. For any studied surfactant, the equilibrium oil solubilization was attained at a very long time (about 24 h). Most of the oil solubilization values at 20 min were around 10-20% of the equilibrium oil solubilization values, suggesting that the washing time used in the washing experiment as well as in actual application is insufficient to approach equilibrium solubilization and most detached oil is in unsolubilized form which is consistent with our previous work [20].

The solubilization of methyl palmitate by SDS and MES with 5 wt% NaCl could not be measured at 15 and 20 °C because these two studied temperatures were below the Krafft temperatures of 23.5±0.5 and 22.5±0.5 °C, respectively. Generally, the Kraft temperature of SDS and MES without NaCl are 16 and 6 °C, respectively [49-51]. The Kraft temperature of anionic surfactants increased in water by increasing concentration of counterion from added NaCl [51, 52].

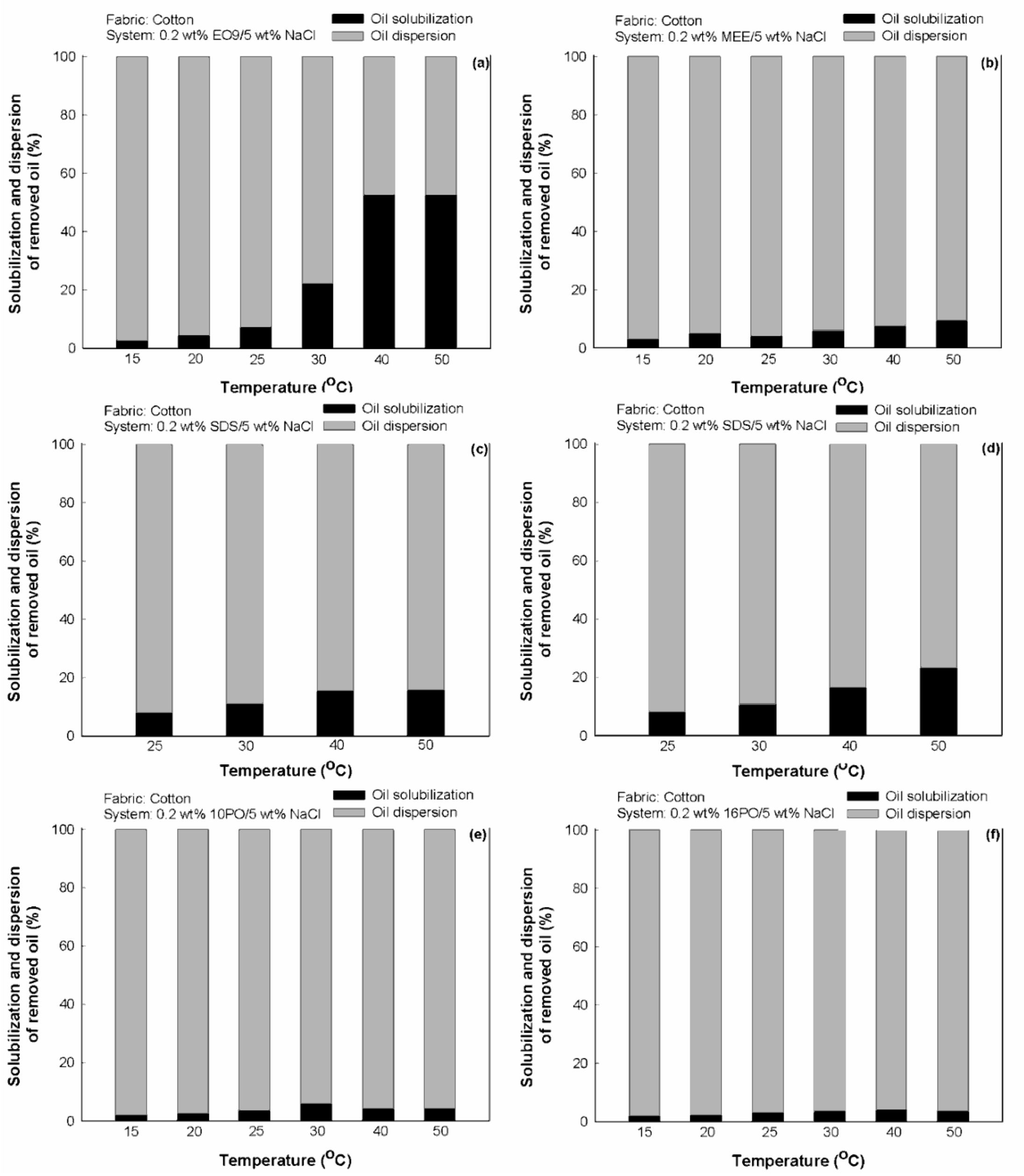

Figure 5.5 The solubilization and unsolubilization portions of removed oil as a function of temperature at a 0.2 wt% total surfactant concentration and 5 wt% NaCl on cotton fabric: (a) EO9, (b) MEE, (c) SDS, (d) MES, (e) $C_{12,14}$-10PO-2EO-SO_4Na, and (f) $C_{12,14}$-16PO-2EO-SO_4Na.

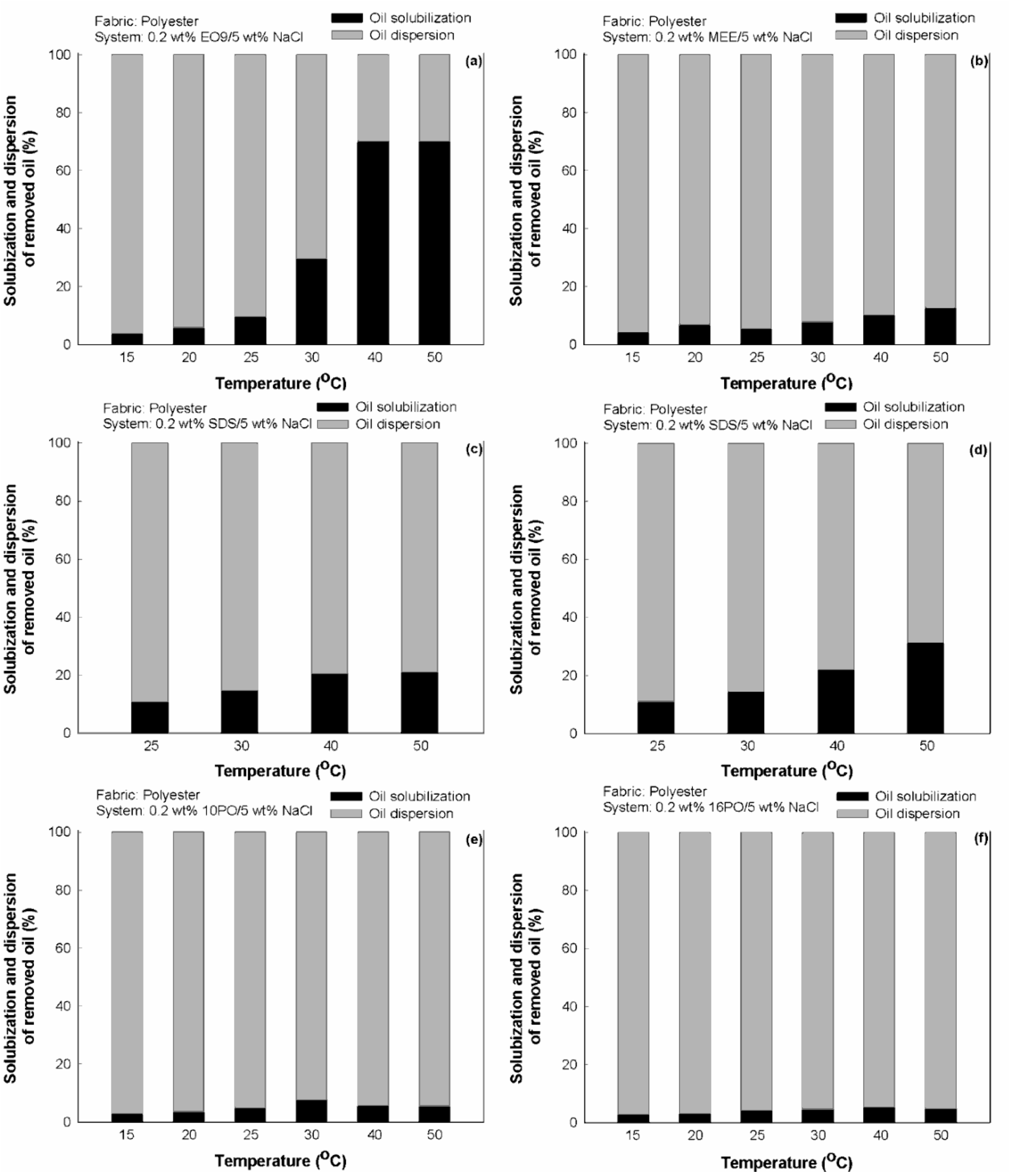

Figure 5.6 The solubilization and unsolubilization portions of removed oil as a function of temperature at a 0.2 wt% total surfactant concentration and 5 wt% NaCl on polyester fabric: (a) EO9, (b) MEE, (c) SDS, (d) MES, (e) $C_{12,14}$-10PO-2EO-SO_4Na, and (f) $C_{12,14}$-16PO-2EO-SO_4Na.

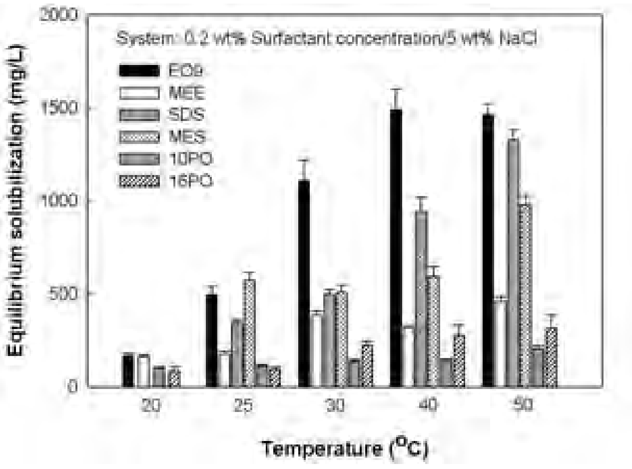

Figure 5.7 The equilibrium oil solubilization of different surfactants as a function of temperature at 0.2 wt% surfactant and 5 wt% NaCl.

Table 5.2 The ratio of oil solubilization at 20 min to equilibrium oil solubilization at different surfactant solutions and temperatures

0.2 wt% EO9/5 wt% NaCl				0.2 wt% MEE/5 wt% NaCl		
Temp.	Oil solubilization (g/L)		Ratio (a/b)	Oil solubilization (g/L)		Ratio (a/b)
(°C)	At 20 min (a)	At equilibrium (b)		At 20 min (a)	At equilibrium (b)	
20	0.0268±0.004	0.1635±0.015	0.1641	0.0314±0.002	0.1609±0.008	0.1950
25	0.0436±0.003	0.4946±0.046	0.0883	0.0253±0.005	0.1726±0.017	0.1463
30	0.1335±0.001	1.1080±0.108	0.1205	0.0360±0.003	0.3840±0.026	0.0938
40	0.3155±0.030	1.4900±0.109	0.2117	0.0465±0.011	0.3150±0.014	0.1476
50	0.3160±0.021	1.4610±0.061	0.2163	0.0570±0.024	0.4570±0.026	0.1247
0.2 wt% SDS/5 wt% NaCl				0.2 wt% MES/5 wt% NaCl		
Temp.	Oil solubilization (g/L)		Ratio (a/b)	Oil solubilization (g/L)		Ratio (a/b)
(°C)	At 20 min (a)	At equilibrium (b)		At 20 min (a)	At equilibrium (b)	
25	0.0482±0.009	0.3430±0.016	0.1404	0.0490±0.016	0.5750±0.041	0.0852
30	0.0665±0.019	0.4970±0.026	0.1338	0.0650±0.047	0.5070±0.038	0.1282
40	0.0925±0.001	0.9400±0.079	0.0984	0.0990±0.019	0.5910±0.053	0.1675
50	0.0950±0.010	1.3280±0.051	0.0715	0.1405±0.008	0.9800±0.045	0.1434
0.2 wt% 10PO/5 wt% NaCl				0.2 wt% 16PO/5 wt% NaCl		
Temp.	Oil solubilization (g/L)		Ratio (a/b)	Oil solubilization (g/L)		Ratio (a/b)
(°C)	At 20 min (a)	At equilibrium (b)		At 20 min (a)	At equilibrium (b)	
20	0.0160±0.001	0.1010±0.004	0.1584	0.0135±0.004	0.0855±0.021	0.1579

25	0.0220±0.002	0.1110±0.008	0.1982	0.0185±0.003	0.0900±0.014	0.2056
30	0.0350±0.011	0.1370±0.011	0.2555	0.0205±0.005	0.2220±0.021	0.0923
40	0.0255±0.004	0.1460±0.005	0.1747	0.0240±0.002	0.2790±0.056	0.0860
50	0.0255±0.001	0.2060±0.017	0.1238	0.0220±0.002	0.3160±0.068	0.0696

5.4.5 Particle Size Distribution of Detached Oil Particles

The particle size distribution and averaged size of detached methyl palmitate particles suspending in the washing solution after 20 min of the wash step of any studied surfactant on both fabrics at 20 ºC are shown in Table 5.3. For all studied surfactants, the particle size distribution of the methyl palmitate solid particles detached from any fabric consisted of three ranges of particle sizes (1–5, 5-100, 100-600 µm). EO9 also shows excellent performance to reduce the particle size of the detached solid methyl palmitate particles as compared to the other surfactants on both studied fabrics. The results suggest that surfactant solution penetrates the methyl palmitate by wetting, the soil is then dislodged as small particles or droplets, so the small particle size correlates well with good wettability leading to the higher oil removal.

Table 5.3 Particle size distribution of methyl palmitate after washing (20 min) in a 0.2 wt% surfactant concentration and 5 wt% NaCl at 20 °C

Washing solution	1–5 µm		5–100 µm		100–600 µm		Mean size (µm)
	Size (µm)	Vol. (%)	Size (µm)	Vol. (%)	Size (µm)	Vol. (%)	
Cotton							
DI water	2.3	9.4	23.2	58.4	282.1	32.2	100.6±4.0
Commercial detergent(CD)	2.3	13.1	22.8	68.5	325.1	18.4	75.6±4.1
EO9	2.4	17.4	14.7	68.0	347.7	14.6	58.6±6.4
SDS	2.1	15.2	18.3	66.3	328.1	18.5	73.0±3.7
MES	2.3	9.5	29.7	67.5	305.9	23.0	90.5±1.2
MEE	2.2	11.3	24.9	71.9	294.8	16.8	67.8±1.7
$C_{12,14}$-10PO-2EO-SO_4Na	2.3	15.7	20.0	64.2	363.3	20.1	86.3±2.4
$C_{12,14}$-16PO-2EO-SO_4Na	2.3	14.5	22.7	65.9	323.2	19.6	78.0±4.1
Polyester							
DI water	2.8	6.5	30.0	57.1	280.6	36.4	119.6±18

Commercial detergent(CD)	2.3	11.8	24.1	65.8	345.5	22.4	93.6±4.4
EO9	2.3	17.4	18.5	68.0	276.9	14.6	42.9±2.6
SDS	2.1	14.5	15.9	68.1	349.2	17.4	71.9±2.6
MES	2.3	10.0	28.1	68.0	293.7	22.0	84.1±4.1
MEE	2.3	10.7	23.6	67.3	321.9	22.0	87.0±1.1
$C_{12,14}$-10PO-2EO-SO_4Na	2.3	15.1	21.3	67.7	310.5	17.2	68.2±5.3
$C_{12,14}$-16PO-2EO-SO_4Na	2.3	14.5	20.6	63.5	368.8	22.0	94.5±2.7

5.4.6 Zeta Potential Versus Dispersion Stability Results

Table 5.4 shows the zeta potential values of methyl palmitate, cotton, and polyester particles in various solution systems at 25 °C. The point of zero charge (PZC) values of methyl palmitate, cotton, and polyester were 2.20, 2.90, and 2.40, respectively, indicating that the net surface charges of these three materials are always negative in detergency study because of all studied surfactant solutions have pH around 6 - 7. The zeta potential of methyl palmitate in all solutions has high magnitude of zeta potential because of the ester functional group in methyl palmitate which is hydrolyzed into carboxyl and hydroxyl groups to provide negative charges [53-56]. The zeta potential values of the studied oil and fabrics in 0.2 wt% commercial detergent without NaCl have the highest values because the main surfactant in commercial detergent is anionic surfactants which are linear alkylbenzene sulphonate (LAS) and sodium lauryl ether sulphate (SLES) having 9 wt% and 10.5 wt%, respectively while nonionic surfactant is ethoxylated alcohol having 2 wt%. This is probably due to the zeta potential of anionic surfactants in commercial detergent. Among studied surfactants, the MES caused all three surfaces to have the highest negative charge as much as 28.3, 28.2, and 24.9 for methyl palmitate, polyester, and cotton, respectively whereas the EO9 and MEE caused all three surfaces to have less negative charge than anionic surfactants. Generally, anionic surfactants play an important role for increasing negative potential charge on both fabrics and soil particles. For nonionic surfactants, the adsorption of nonionic onto both surfaces does not significantly increase its electrical potential and ineffective as anionic for removal of particulate soil [48, 53]. However, nonionic surfactants produce steric barriers for prevention of soil redeposition.

Figure 5.8 shows the correlation between the zeta potential and dispersion stability (in term of average absorbance) of methyl palmitate in 0.2 wt% surfactant and 5 wt% NaCl concentrations as a function of surfactant types as compared to the commercial detergent and DI water at 25 °C. We speculated that the higher absolute zeta potential, the higher electrostatic repulsion could be an important factor for higher dispersion stability [48, 57]. The higher the absorbance, the higher the dispersion stability. The results of zeta potential show that both the commercial detergent and DI water caused the higher negative charged which is an opposite trend with the lower dispersion stability. For the studied surfactant solution, the highest negative charge was MES but the highest dispersion stability was the extended surfactant. However, the presence of surfactant improved the dispersion stability as compared to DI water despite the fact that the zeta potential of DI water is much more negative charge because of 5 wt% NaCl in surfactant solution causing the zeta potential of methyl palmitate became less negative, due to compression of the double layer or reduction of Debye length next to the surface with the ionic strength [58, 59]. In a comparison among studied surfactants, SDS had the lowest dispersion stability, corresponding to the highest oil redeposition at below the oil melting point as shown in Fig.5.3a-2 which is consistent with literature [60] that sodium dodecyl sulfate (SDS) had the worst dispersion stability. According to these results, zeta potential increase does not correspond to increasing dispersion stability or detergency. Therefore, electrostatics is not a dominant mechanism for solid non-particulate soil detergency.

Table 4 Zeta potential of methyl palmitate (oil), polyester, and cotton in different surfactant solutions at a 0.2 wt% surfactant concentration, 5 wt% NaCl, and 25 ºC

Surfactant solution	Zeta potential (mV)		
	Oil	Polyester	Cotton
DI water	–46.2±2.7	–50.0±5.0	–20.3±5.0
Commercial detergent(CD)	–65.9±2.7	–69.5±4.1	–64.0±3.3
EO9	– 5.7±0.9	– 8.8±1.0	– 5.7±1.2
SDS	–18.3±1.7	–16.4±2.1	–14.1±1.0
MES	–28.3±1.7	–28.2±2.2	–24.9±2.2

MEE	– 5.6±1.0	– 4.4±0.3	– 3.4±0.5
$C_{12,14}$-10PO-2EO-SO_4Na	–27.3±2.9	–13.2±0.9	–11.9±1.3
$C_{12,14}$-16PO-2EO-SO_4Na	–15.1±1.7	–11.0±1.8	– 9.1±1.1

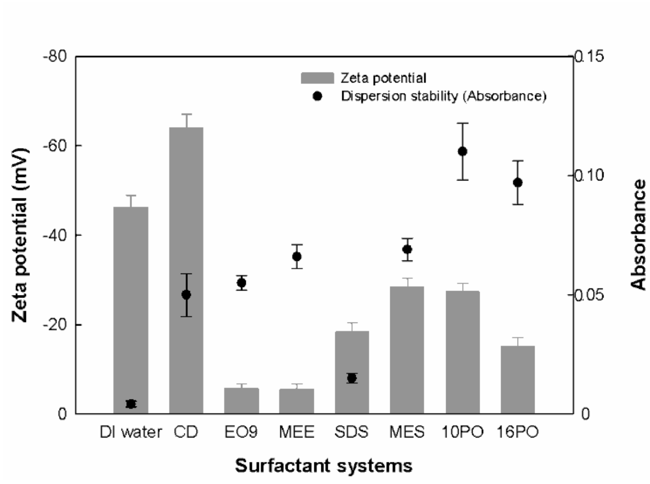

Figure 5.8 The zeta potential and dispersion stability in terms of absorbance of solid methyl palmiate particles in various surfactant systems at 25 °C. A surfactant concentration at 0.2 wt%, and 5 wt% NaCl.

5.4.6 Detergency Performance: Effect of Soiling Procedure

Since the detergency performance of solid non-particulate soil depends on how soil deposited on the fabrics or the soiling effect. Therefore, the effect of soiling procedure was measured by heating the soiled swatches above the melting point and then cooling again before doing the detergency experiment, so the soil is liquefied and diffuses into the fabric fibers. The effect of soiling procedure on detergency performance as a function of washing temperature on both studied fabrics for a number of surfactant systems and DI water is shown in Fig. 5.9. The surfactant concentration was 0.2 wt% and 5 wt% NaCl concentration. The results show that the oil removal of the heated soiling, at any given washing temperature, was considerably lower than that of not heated soiling for both DI water solution and all studied surfactant systems specially, at below the melting point. For DI water system, below the melting point, the oil removal was lower than that of no heated soiling around 15 – 20 % for both studied fabrics and at above the melting point, the oil removal was decreased about 5% for polyester and 13% for cotton. For the use of surfactant systems of heated soiling effect, the oil removal markedly decreased 40 – 55 % below the melting point on both studied fabrics and at above the melting point for both studied fabrics, it decreased around 15 – 30 % for EO9 and MEE and 5 – 15 % for SDS and MES. This was attributed to the diffusion of liquid oil into the interior of fabrics at high temperatures where it becomes poor contact with the surfactant solution. Fort et al. [44] found similar results that high washing temperature increased both the rate of detergency performance and the diffusion of fatty soils into inside the polymer interior in which the soils inaccessible with the surfactant solution leading to difficult to be removed. However, the detergency performance of heated soiling on both studied fabrics showed a similar trend to the detergency performance of not heated soiling for all systems with increasing detergency efficiency. Therefore, soiling procedure is an important effect to detergency efficiency of solid non-particulate soil.

In conclusion, detergency of solid non-particulate soil is a complex process which has many mechanisms and several factors involved. Many studies and researches proposed roll up, emulsification, and solubilization mechanisms of oily soil removal from fabrics as a dominant mechanism due to the low oil/water IFT [13-19, 23-25]. From this work, it found that most of the detached methyl palmitate is unsolubilizied form either washing temperatures as a solid particles or liquid droplets. Therefore, a new proposed mechanism of solid non-particulate soil detergency is the dispersion of detached oil particles in washing solution beginning with the contact angle of surfactant solution onto a flat solid non-particulate soil surface leading to the reduction of surface tension between solid non-particulate soil and surfactant solution. According to the results, the surfactant solution is better able to penetrate into inter-particle clusters and crevices leading to most of the dislodged solid oil particles suspended in the wash solution [3, 7, 20, 61, 62] by repulsive force between charged particles of the adsorbed surfactant molecules. Therefore, wetting by contact angle, dispersion stability, and particle size are important parameter to be a predictor of good detergency below the melting point. For the future, soiling procedure effect with different condition should be investigated to obtain the optimized condition for improving and enhancing the detergency performance of solid non-particulate soil, especially at low washing temperature.

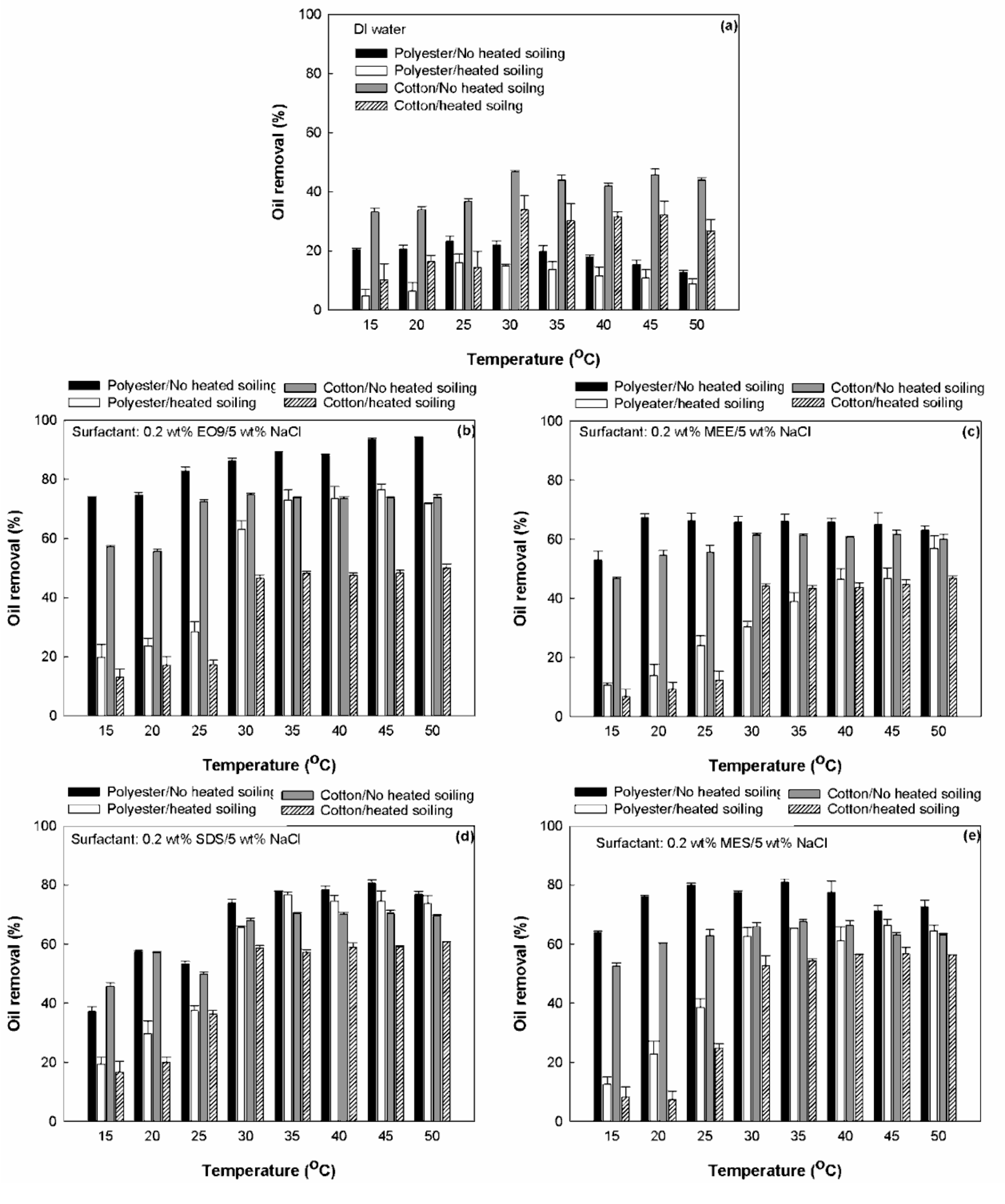

Figure 5.9 Detergency performance as a function of washing temperature of different systems; (a) DI water, (b) EO9, (c) MEE, (d) SDS, (e) MES on both polyester and cotton fabrics (washing conditions: a surfactant concentration of 0.2 wt%, a NaCl concentration of 5 wt% and two soiling temperatures of 25 and 40 °C.

5.5 Acknowledgments

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CHAPTER VI
LAUNDRY DETERGENCY OF SOLID NON-PARTICULATE SOIL USING MICROEMULSION-BASED FORMULATION

6.1 Abstract

Laundry detergency of solid non-particulate soil on polyester and cotton was investigated using a microemulsion-based formulation, consisting of an anionic extended surfactant ($C_{12,13}$-4PO-SO_4Na) and sodium mono-and di-methyl naphthalene sulfonate (SMDNS) as the hydrophilic linker, to provide a Winsor Type III microemulsion with an ultralow interfacial tension (IFT). In this work, methyl palmitate (palmitic acid methyl ester) having a melting point around 30 °C, was used as a model solid non-particulate (waxy) soil. A total surfactant concentration of 0.35 wt% of the selected formulation (4:0.65 weight ratio of $C_{12,13}$-4PO-SO_4Na:SMDNS) with 5.3 wt% NaCl was able to form a middle phase microemulsion at a high temperature (40 °C),which provided the highest oil removal level with the lowest oil redeposition and the lowest IFT, and was much higher than that with a commercial detergent or de-ionized water. Most of the detached oil, whether in liquid or solid state, was in an unsolubilized form. Hence, the dispersion stability of the detached oil droplets or solidified oil particles that resulted from the surfactant adsorption played an important role in the oil redeposition. For an oily detergency, the lower the system IFT, the higher the oil removal whereas for a waxy (non-particulate) soil detergency, the lower the contact angle, the higher the solidified oil removal. For a liquefied oil, the detergency mechanism was roll up and emulsification with dispersion stability, while that for the waxy soil (solid oil) was the detachment by wettability with dispersion stability.

Keywords Solid non-particulate soil, Microemulsion, Detergency, Extended surfactant

6.2 Introduction

Several studies of detergency have been conducted in order to gain a better understanding of the detergency mechanisms for both oily[1-6)] and particulate[7,8)] soils. However, there are only a few reports on the cold-water detergency when the stained oils on the fabric have solidified. Solid non-particulate soils, or solid fat soils, are a special type of soil in which the substances have properties between a liquid and solid, such as butter, margarine and solidified hamburger grease, depending on temperature. These types of soil are a challenging problem for detergent formulations, especially in cold climate regions where the semi-solid/oily soil is hard to remove from the fabrics. Kawase *et al.*[9,10)] found that the dominant mechanism of solid fatty acid soil detergency at a low washing temperature was solubilization by using both nonionic and anionic surfactants. The kinetic of solid fatty acid solubilization consisted of five steps; first, surfactant aggregates to diffuse to the surface of the fatty acid, second, the aggregates to adsorb on the surface of the fatty acid, third, fatty acid molecules to diffuse into the micelles, fourth, aggregates containing fatty acid and surfactant to desorb from the surface or called breaking up, and fifth, the mixed aggregates to diffuse away from the surface.

Microemulsions are an isotropic, thermodynamically stable system that consists of water, oil and surfactants. The immiscible water and oil liquids can merge partially or totally into a single phase under appropriate conditions. There are four types of microemulsions, the Winsor Type I, II, III and IV, which depend on various factors, including the type and concentration of surfactants, temperature for nonionic surfactants and salinity for ionic surfactants. When a Winsor Type III microemulsion is formed, it has the two important unique properties of a very high oil solubilization and a very low oil-water interfacial tension (IFT)[11)]. Hence, microemulsion-based formulations have become of great interest in the area of detergency[12)]. Tongcumpou *et al.*[1-3)] studied the relationship between microemulsion phase behaviors and oily soil detergency, along with the effects of the surfactant composition, temperature and salinity on the detergency performance. They found that the transition of microemulsion phases induced by the salt scan technique could be observed for both hexadecane and motor oil systems. In addition, the use of surfactant mixtures containing an anionic surfactant (highly hydrophilic) and two nonionic surfactants (intermediate and highly hydrophobic) could make the systems become more robust with respect to the temperature, compared to single-surfactant systems. In the Winsor Type III or middle phase microemulsion region, the detergency performance was much higher than that in either the Winsor Type I or Type II microemulsion regions. Under the middle phase microemulsion condition, the level of oil removal in the wash step was not very high due to the spreading effect as a result of the ultralow IFT. However, a significant oil removal (as high as that in the wash step) was found in the rinse step because the increase in the system IFT passed the composition at which the rollup mechanism gave additional oil removal. Tongcumpou *et al.*,4) who studied triolein removal using a microemulsion-based formulation with mixed surfactants, reported that there were two values of maximum oily detergency in the salinity range from 0.1–10 wt% NaCl. The higher the hydrophilicity of the system, the higher the salinity level that was required for maximum detergency. The first maximum peak resulted from a spreading or wetting effect, while the second maximum detergency was related to the ultralow IFT associated with the oil/water middle-phase microemulsion formation. A triolein removal of >80% was achieved by the microemulsion-based formulation. According to the Winsor R-concept, an effective way to form microemulsions with greater solubilization and lower IFT is to equally increase the interaction of the surfactant for both oil and water, which can be achieved by increasing both the hydrophilicity of the surfactant head and the hydrophobicity of the hydrocarbon tail. However, this approach is limited by the reduced solubility with the increasing length of the hydrocarbon tail. Hence, extended surfactants have been proposed as an alternative surfactant structure to facilitate the formation of a Winsor Type III microemulsion without reducing the water solubility13,14).

An extended surfactant has a group of intermediate polarity, such as polypropylene oxide (PO) or PO-polyethylene oxide (PO-EO) groups, inserted between the hydrophilic head group and the hydrocarbon tail group. As a result, it can further stretch out into both the oil and aqueous phases, resulting in a smoother transition between the hydrophilic and hydrophobic regions at the interface. The addition of a PO group in the hydrocarbon tail of a surfactant molecule gives a more hydrophobic portion to extend the tail into the oil phase yet still maintains a good interaction with the water phase. Hence, it becomes easy to form a middle-phase microemulsion, which provides both a high solubilization and ultralow IFT, leading to various applications, especially detergency$^{15-18)}$. Tanthakit *et al.*$^{19)}$ investigated palm oil removal from fabrics using microemulsion-based formulations based upon a mixed surfactant system of $C_{14,15}H_{29,31}(PO)_3SO_4Na$, as an anionic extended surfactant, and a secondary alcohol ethoxylate ($C_{12,14}H_{25,29}O(EO)_5H$), as a nonionic surfactant, at different weight ratios in order to obtain a proper hydrophilic-lipophilic balance (HLB). The oil removal by the surfactant blend could exceed 90%, which was greater than those of either component surfactant alone or a commercial liquid laundry detergent. Phan *et al.*$^{20)}$ investigated the use of a single extended surfactant for microemulsion-based detergency of vegetable oils and reported that good canola oil detergency (>80%) was achieved at 25°C using a very low surfactant concentration of 125 ppm. Do *et al.*$^{21)}$ reported that a mixture of a linear extended surfactant (C_{10}-$(PO)_{18}$-$(EO)_2$-SO_4Na) and a hydrophobic twin-tailed sodium dioctylsulfosuccinate surfactant showed synergism in a Winsor type III microemulsion formation, leading to a high detergency performance of vegetable oils and semi-solid fats at a low salinity and a low washing temperature. Attaphong *et al.*$^{22)}$ studied the relationship of microemulsion formation of an extended surfactant and canola oil detergency at a low surfactant concentration and low washing temperature, and found that a good detergency performance at a low washing temperature corresponded with a lower IFT.

In our previous work$^{23)}$, methyl palmitate or palmitic acid methyl ester was used as a model of solid non-particulate soil being removed from two tested fabrics of cotton and polyester by using a single anionic extended surfactant at temperatures below and above the soil’s melting point. The experiments were carried out to find out the optimum concentrations of the surfactant and NaCl for the maximum removal of methyl palmitate at high temperatures (higher than the melting point) and low temperatures (lower than the melting point) which they were found to be not the same formulations. The study results revealed that the lower the contact angle, the higher the soil detergency. In addition, most of removed oil was in a unsolubilized form for either solid particles or liquid droplets. In general, mixed surfactant systems provide a higher oil solubilization than single surfactant systems[1)] and so surfactant-based microemulsion formulation was employed in this study. The aim of this research was to investigate a use of microemulsion-based formulation for non-particulate or waxy soil detergency. An extended surfactant (a branched alkyl polypropoxylated sulfate, $C_{12,13}$-$(PO)_4$-SO_4Na) and sodium mono- and di-methyl naphthalene sulfonate (SMDNS) as a hydrophilic linker were selected to form a Winsor Type III microemulsion at 40 °C. This microemulsion-based formulation was further applied to remove methyl palmitate from fabrics at a temperature below the melting point (and so where the methyl palmitate was in a solid state). It was hypothesized that this microemulsion-based formulation was also good for non-particulate or waxy soil detergency.

6.3 Experimental Procedures

6.3.1 Materials

Methyl palmitate or palmitic acid methyl ester (99.8% purity) was purchased from Sigma-Aldrich (BKK, Thailand). The pure cotton and pure polyester fabrics were supplied by Testfabrics, Inc. (Middlesex, NJ, USA). The extended surfactant ($C_{12,13}$-$(PO)_4$-SO_4Na), a branched alcohol propoxylate sulfate sodium salt with 12-13 carbon numbers and approximately four PO units, had an active content of 30 wt% and was donated by Sasol North America (Lake Charles, LA). Sodium mono- and dimethyl naphthalene sulfonate (SMDNS) with an active content of 45–55 wt% , was purchased from CKWitco (Houston, TX). Commercial detergent (Breeze® excel liquid detergent), a leading brand was purchased from a local market and used for comparison purposes. Oil red O (solvent Red 27, No. 26125) was bought from the Aldrich Chemical Company, Inc. and sodium chloride (NaCl) was purchased from LabScan Asia Co., Ltd. De-ionized (DI) water was used to prepare all solutions.

6.3.2 Experimental Procedures

6.3.2.1 Microemulsion Formation

Phase studies were performed by preparing different aqueous surfactant concentrations. The aqueous surfactant solution and oil were added at a 1:1 (v/v) ratio to a series of 15-ml flat-bottomed screw-capped tubes[1,19,20,24). Extended surfactant mixture systems were formulated at a high surfactant concentration of 4 wt% with different concentrations of SMDNS from 0–1% and different NaCl concentrations in order to find a minimum hydrophilic linker and salinity for formation of a Winsor Type III microemulsion. All tubes were gently shaken and left in a water bath for two weeks to ensure equilibrium before evaluating the microemulsion type and measuring the phase heights at 40 °C. The height of each liquid phase in each vial was measured by using a cathetometer (model TC-II from Titan Tool Supply, Inc.) attached to a digital height gauge (model 192-631) obtained from Mituyo with an accuracy of 0.001 mm. The schematic of the experiment for microemulsion formation is shown in Figure 6.1.

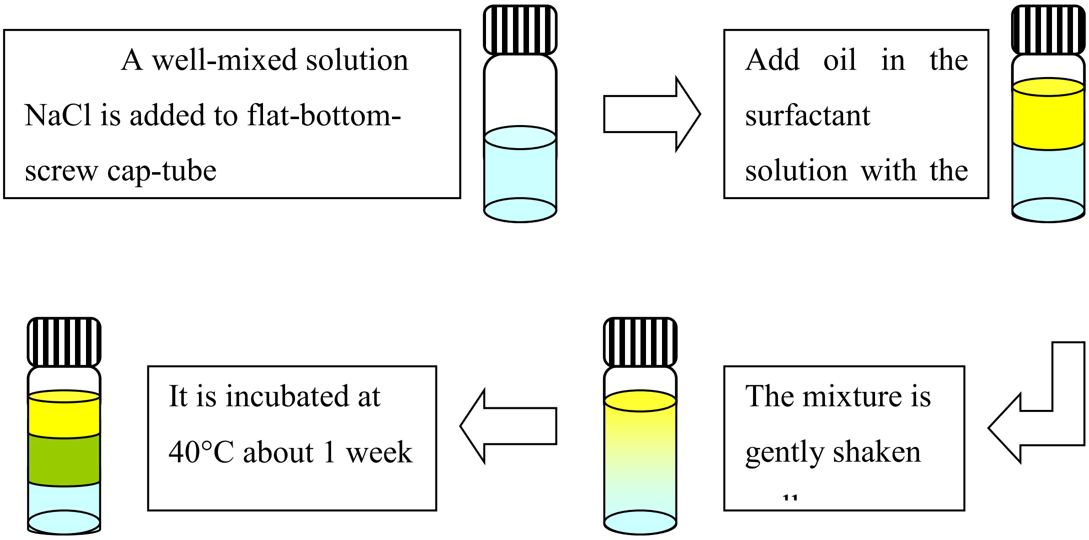

Figure 6.1 Schematic experiment of microemulsion formation.

6.3.2.2 Fish Diagram Study

Microemulsions were classified by both visual observation at high surfactant concentrations and dynamic IFT values at low surfactant concentrations, where the volume of the middle phase was difficult to be visually observed. The data of identified microemulsion types were used to construct a fish diagram, which is a graph of the total surfactant concentration vs. the NaCl concentration[19)]. Fish diagrams are generally used to determine the minimum surfactant concentration required to form a Winsor Type III microemulsion, which is known as the critical microemulsion concentration (CμC). Moreover, the intersection between the microemulsion regions (Winsor's Types I, II, III and IV) shows the solubilization capacity of the system to obtain a single phase of microemulsion (Winsor Type IV)[14,25,26)].

6.3.2.3. Fourier Transform Infrared (FT-IR) Spectroscopy

The powdered methyl palmitate particles were characterized for their functional groups by FT-IR spectroscopy (Nicolet Nexus, 670). The specimens were prepared by grinding with dry potassium bromide as a nonabsorbent medium. The mixture was packed into a sample holder and pressed to form a disk. The spectra were recorded over a wave number range of 4000–400 $cm^{-1}$with 64 scans at a resolution of 4 cm^{-1}.

6.3.2.4 Fabric Pretreatment and Detergency Experiment

The swatches (polyester and cotton fabric samples) having a size of (3×4) inches was prewashed before soiling to get rid of the residues of mill finishing agents. The prewashing was performed with 1000 mL of distilled water, a 10-min wash cycle with an agitation speed of 120 rpm by using a terg-o-tometer (Copley, DIS 8000). After the prewashing step, the swatch was left to dry overnight at room temperature. This method was followed according to the ASTM standard guide D4265-98[27)]. Approximately 0.1 g of the oil-soluble dye was added to 100 mL of the oil above its melting point. The colored oil was filtered until clear. Next, 10 mL of the clear dyed oil was diluted with dichloromethane to 100 mL[28)]. After that, the prewashed swatch was immerged into a container which containing the dyed oil solution for a specific time. Finally, the soiled swatches were left to dry overnight at room temperature. All swatches were freshly prepared for each batch of laundry experiments. The laundry experiments were conducted using the same a terg-o-tometer, which simulates a home washing-machine action in a bench scale unit. The experimental procedure consisted of a wash step for 20 min with 1000 mL of a surfactant washing solution and two rinse steps for 2 and 3 min with 1000 mL of DI water. An agitation speed for each step was fixed at 120 rpm. Three soiled swatches and one unsoiled swatch for anti-redeposition testing were washed in each bucket for one cycle for replication.

6.3.2.5 Oil Removal Measurement

Oil removal was calculated based on residual oil on the swatches to be washed off during the detergency experiment. The amount of residual oil was extracted by submerging a swatch in isopropanol for 24 h at room temperature, and then the extracted solution was analyzed by an ultraviolet/visible spectrophotometer (Hewlett-Packard, 8452A)[19,28]. The oil removal was calculated from subtracting the remaining oil residue after washing from the original oil content in each swatch.

6.3.2.6 Oil Solubilization Measurement

An excess quantity of methyl palmitate was added to the mixed surfactant solution having a total surfactant concentration of 0.35 wt% prepared from the selected formulation and a NaCl concentration of 5.3 wt%. The mixture was stirred at 120 rpm for 20 min at different temperatures to simulate the wash step of the washing experiment. The surfactant solution phase was taken to analyze for total carbon content by using a Total Organic Carbon Analyzer (TOC) (Shimadzu, TOC 5000). to represent the total organic carbon of the surfactants and methyl palmitate. The concentration of methyl palmitate representing the amount of methyl palmitate solubilized in micelles was obtained from subtracting the total carbon content by the total carbon of the surfactants.

6.3.2.7 Oil Dispersion Stability Measurement

The dispersion stability of methyl palmitate solid particles dispersed in an aqueous solution containing 0.35 wt% of the selected formulation with different NaCl concentrations at 25 °C (below the melting point) was determined by measuring absorbance as a function of time using a UV–Visible spectrophotometer (Hewlett-Packard, 8452A). The solution was prepared by adding the methyl palmitate particles in the surfactant solution, after being well mixed; the prepared solution was transferred to a spectrophotometer cuvette. The reading of absorbance was fixed at a wavelength of 550 nm and was recorded every 10 s for 2 h. The absorbance values in the range of 2000 – 5000 s were averaged to represent the dispersion stability. The higher the absorbance, the higher the dispersion stability.

6.3.2.8 Detergency and Measurement Methods

The measurements of CMC, IFT, particle size distribution, contact angle, and zeta potential were similar to the methods described in our previous study[23)].

6.4 Results and Discussion

6.4.1 Microemulsion Phase Behavior of Methyl Plamitate

For the preliminary evaluation of the microemulsion phase behavior, the concentration of $C_{12,13}$-$(PO)_4$-SO_4Na was fixed at 4wt% while the concentration of SMDNS was varied. A minimum SMDNS concentration of 0.65 wt% was required to achieve the formation of a Winsor Type III microemulsion (Data not shown here). Hence, the mixture of $C_{12,13}$-$(PO)_4$-SO_4Na and SMDNS with concentrations of 4 and 0.65 wt%, respectively, was used for to constract the Fish diagram of the surfactant system at 40 °C, which is above the oil's melting point of 30 °C, as shown in **Fig. 6.2**. The microemulsion phase behavior was not investigated at very high total surfactant concentrations, where a Winsor Type IV region would exist, because of cost reasons for detergency application. Since the hydrophilic linker was used to improve the interaction at the interface between the surfactant and water phase, an addition of NaCl was needed to maximize the surfactant adsorption at the interface. The triangle in dotted line in the region of middle phase microemulsion (Winsor Type III) enclosed by the phase boundaries (the circle in solid line) indicated the optimum salinity that corresponded to equal volumes of oil and water being solubilized. The lowest surfactant concentration at which the Type III microemulsion forms is known as the critical microemulsion concentration or CμC.

The CμC value of this system was 0.015 wt% at 5.3 wt% NaCl which is consistent with the result of previous study[20)].

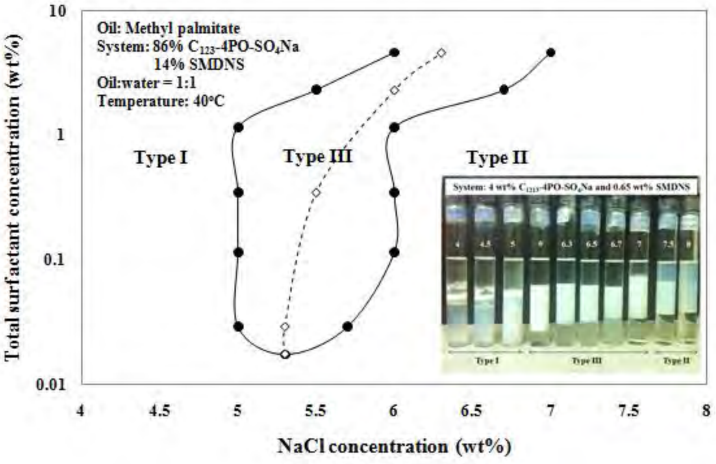

Figure 6.2 Fish diagram of methyl palmitate, extended surfactant ($C_{12,13}$-4PO-SO_4Na), and sodium mono- and dimethyl naphthalene sulfonate (SMDNS) as a function of NaCl concentration at 40 ºC.

The salinity scan phase study of methyl palmitate of the selected formulation (4 wt% $C_{12,13}$-$(PO)_4$-SO_4Na and 0.65 wt% SMDNS) was performed at a 1:1 (v/v) surfactant solution: oil ratio at 40 °C. The plots of volume fractions vs. salinity concentration of different equilibrium times are shown in **Fig. 6.3**, where the height of middle phase microemulsion was not stable and eventually disappeared after two months. This was believed to result from thermal degradation of the surfactant. For example, the changes in the FT-IR spectra of the functional groups after 2 months at different temperatures (**Fig. 6.4**) support the thermal degradation of methyl palmitate after 2 months at a 40 °C or higher.

It is worthwhile to point out that the thermal degradation of methyl palmitate did not affect the detergency performance at high washing temperatures used in this study. According to FTIR results, all functional groups of methyl palmitate did not change with time (up to 60 min) at 40 °C (data not shown here) while the time for the wash step was only 20 min.

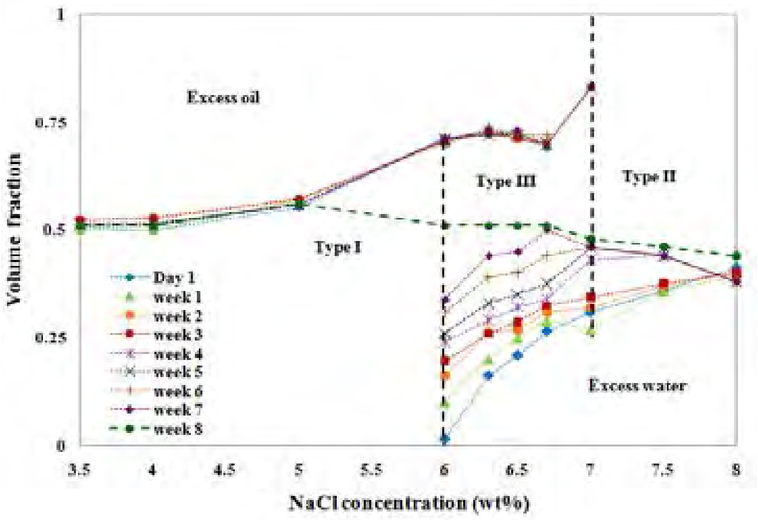

Figure 6.3 Phase height fraction of methyl palmitate and surfactant system between 4 wt% extended surfactant ($C_{12,13}$-4PO-SO_4Na), and 0.65 wt% sodium mono- and dimethyl naphthalene sulfonate (SMDNS) as a function of NaCl concentration and equilibrium times at an initial oil-to-water volumetric ratio of 1:1 at 40 ºC.

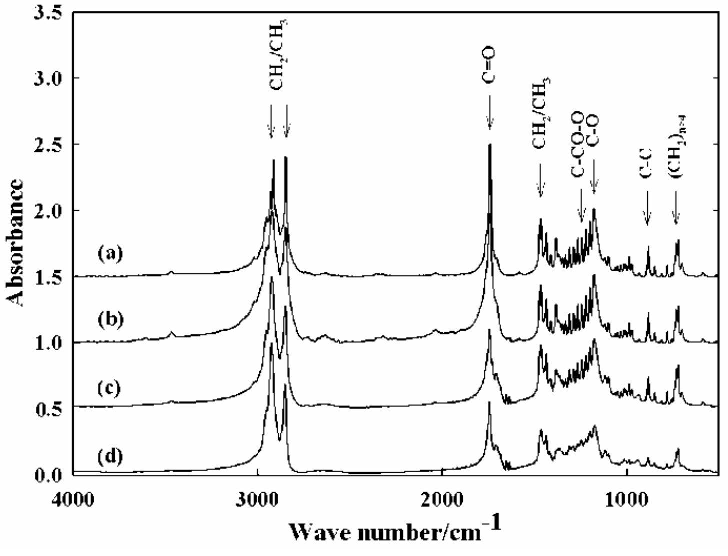

Figure 6.4 FT-IR spectra of methyl palmitate at (a) 20°C, (b) 30°C, (C) 40°C and (d) 50°C for 2 months.

6.4.2 Detergency Performance: Effect of Total Surfactant Concentration

Figure 6.5 shows the oil removal from the polyester and cotton fabrics and its redeposition as a function of the total surfactant concentration at 40 °C (above the oil's melting point). The total surfactant concentration was varied by diluting the selected formulation. The total oil removal increased with increasing total surfactant concentration to reach a plateau at around a 0.35 wt% total surfactant concentration with a maximum oil removal of 65 and 70% for the polyester and cotton fabrics, respectively, which are in good agreement with a previous study[23)]. This is likely explained by the fact that the cotton fabric contains highly polar hydroxyl groups (OH) to hydrogen-bond with water molecules, causing a swelling of the fibers[29)]. Consequently, it lowered the oil-cotton surface interaction, and increased the amount of surfactant adsorbed onto the cotton surface. The amount of oil redeposited on both the fabrics decreased with an increasing total surfactant concentration reaching a minimum when the total surfactant concentration was around 0.1 wt%. The results indicated that the surfactant can help the detached oil particles disperse into the washing solution and so prevented oil redeposition onto the fabric.

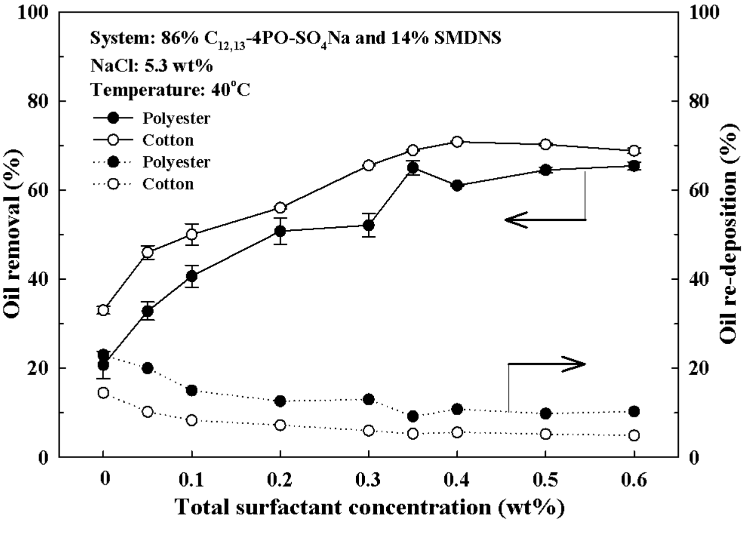

Figure 6.5 Detergency performance as function of total surfactant concentration and relation to oil re-deposition at 40 °C on both test fabrics of cotton and polyester.

6.4.3 Detergency Performance: Effect of Salinity

The effect of salinity on the oil removal and redeposition when using a total surfactant concentration of 0.35 wt% at either 20 or 40 °C, when the methyl palmitate was in solid and liquid state, respectively, is shown in **Fig. 6.6**. The detergency results at 40 °C showed that the level of oil removal was markedly increased with increasing salinity and reached a maximum oil removal of 68% and 75% for the polyester and cotton, respectively, with 5.3 wt% NaCl, corresponding to the formation of a Winsor Type III microemulsion. At 20 °C, which is below the oil melting point (30 °C), the level of oil removal (detergency efficiency) was around 30% and 40% for the polyester and cotton, respectively, which was much lower than at 40 °C for both fabrics. Moreover, the effect of added NaCl on the removal of the solidified oil (at 20 ºC) was negligible for both test fabrics.

The oil redeposition on both test fabrics did not significantly change with changes in the NaCl concentration (**Fig. 6.6b**). For any test fabric, the oil redeposition at 40 °C was lower than that at 20 °C, while the oil redeposition on the cotton was lower than that on the polyester at any given NaCl concentration at both temperatures. This was attributed to the hydrophobicity of oil to adsorb preferably onto the hydrophobic surface of the polyester fabric, as compared to the hydrophilic surface of the cotton fabric.

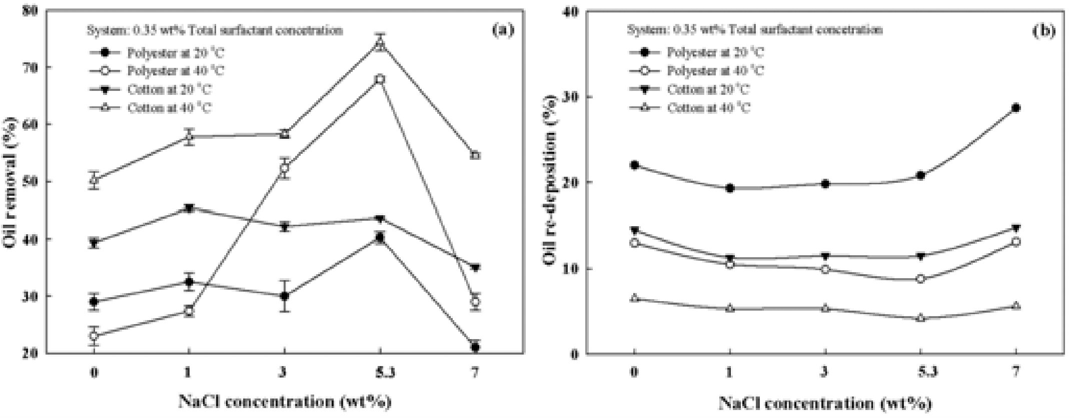

Figure 6.6 Oil removal and redeposition as a function of the NaCl concentration at a temperature below (20 ºC) and above (40 ºC) the oil melting point (30 ºC) on the cotton and polyester fabrics using the selected formulation at 0.35 wt%.

The effect of NaCl concentration on the critical micelle concentration (CMC) of the selected formulation at 25 and 40 °C is shown in **Fig. 6.7a**.When NaCl was increased from 0 to 1 wt% , the CMC value markedly decreased at both temperatures and then declined slightly further with higher NaCl concentrations up to 7 wt% (highest tested), which is consistent with previous reports[15,18]. This likely reflects the reduction in the electrical repulsion between the head groups of the surfactant by counter ion adsorption, causing more surfactant molecules to form micelles and a reduction in the CMC. Moreover, the CMC value at 25 °C was slightly higher than that at 40 °C for all NaCl concentrations except 0 wt% , suggesting that the CMC value is relatively independent of the temperature[30]. An increase in the temperature causes the hydration of the hydrophilic head group, which favors micellization and also increases the disruption of the water structure surrounding the hydrophobic tail group that disfavors micellization. Thus, the effect of temperature on the CMC becomes insignificant[31]. Moreover, the PO groups of the extended surfactant inserted between the hydrophilic head group ($-SO_4^{2-}$) and the hydrophobic tail group (C_{12-13}-), make this extended surfactant less sensitive to temperature than conventional anionic surfactants[16]. The CMC data were also plotted as the logarithm of the CMC vs. the logarithm of total concentration of counter ion (Na^+) at 25 and 40 °C to give the linear Corrin-Harkins plot (**Fig. 6.7b**)[32]. The absolute value of the slope from the plot represents the fractional counter ion binding to micelles, and was 0.31 at 25 °C and 0.29 at 40 °C. These values are consistent with those previously reported[23]. The very small difference between these two values indicates that the fractional counter ion binding on micelles had only slight temperature dependence.

Interestingly, the total surfactant concentration of 0.35 wt% of the selected formulation with 5.3 wt% NaCl in the washing solution used for the detergency experiment is located in the Winsor Type III region which is higher than the CμC (0.015 wt%) and much higher than the CMC (0.001 wt%). Therefore, it can be concluded that the dilute surfactant concentration used in the washing solution could still form the middle phase microemulsion and it also showed a high detergency performance on both studied fabrics, especially at high washing temperatures (see Fig. 6.9).

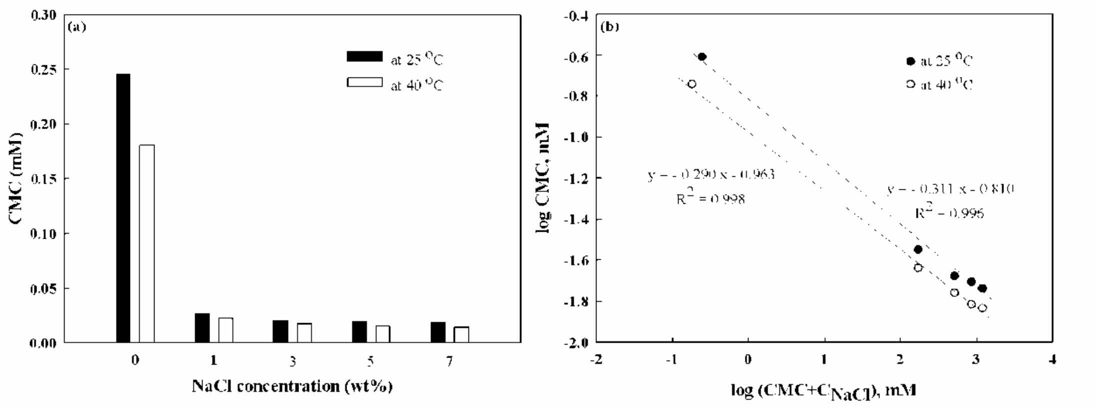

Figure 6.7 The (a) CMC of the selected formulation at 25 °C and 40 °C and (b) Corrin and Harkins plot of selected formulation from the CMC data at 25 °C and 40 °C.

6.4.4 Contact Angle Results

The contact angle is used to indicate the wettability of a solution on any surface, which is first step of a detergency process. The contact angle of the 0.35 wt% selected formulation on the surface of methyl palmitate at 25 °C decreased with increasing NaCl concentration and reached a minimum value (best wetting) of ca. 36° at 5.3 wt% NaCl (**Fig. 6.8**). The increased NaCl concentration causes to a reduction in the repulsive force between the head group of the surfactant molecules by the Na^+ counter ion effect, leading to an increase in the surfactant adsorption. As a result, the contact angle became lower, indicating better wettability. Interestingly, a decrease in the contact angle (higher wettability) corresponded to an increased level of oil removal. As a result, a lower contact angle improves the penetration of the surfactant solution into the inter-particle clusters and crevices, leading to better detergency performance. Thus, a good correlation between the oily detergency performance and contact angle was obtained is this present study, in good agreement with previous studies[23,33)].

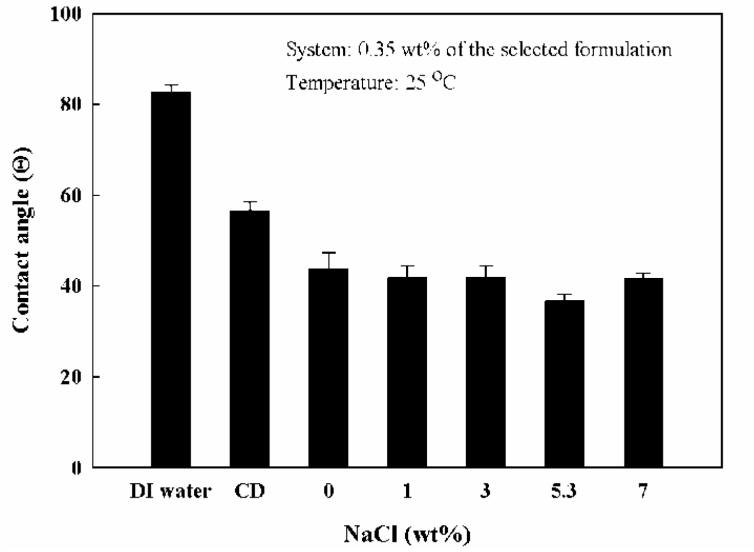

Figure 6.8 The contact angle of the 0.35 wt% selected formulation on the methyl palmitate surface at 25 °C as a function of the salinity.

6.4.5 Effect of Temperature on Detergency Performance

The oil removal and redeposition on both studied fabrics as a function of the washing temperature using the selected formulation at the total surfactant concentration of 0.35 wt% , in comparison to that with DI water or the commercial detergent, is shown in **Fig. 6.9**. The oil removal increased with an increasing washing temperature for the polyester fabric, whereas the oil removal from cotton was significantly increased when raising the temperature from 30 to 35 °C with an efficiency increase from 59 to 78% , and thereafter the detergency performance remained almost unchanged in the range of 78-80% . In comparison with the commercial detergent and DI water, for any given washing temperature, the total oil removal of the selected formulation was much higher, especially on the polyester fabric. At a washing temperature below the oil' s melting point of 30 °C the detergency performance using the selected formulation was significantly reduced to a range of 45–55% for the polyester and 40–60% for the cotton. Generally, an increased temperature caused a reduced solution viscosity and IFT,which enhanced the oil removal. The lower oil removal at a washing temperature below the melting point, as compared to that above the melting point, can be explained by the fact that the solidified methyl palmitate had a stronger interaction with the fabric surface than the liquefied methyl palmitate.

The oil redeposition of any system showed the opposite trend to the oil removal on both test fabrics (**Fig. 6.9c and d**). In all washing solutions, the oil redeposition trended to decrease with increasing washing temperature below the melting point. At around the melting point, the oil redeposition seemed to reach a minimum. Beyond the melting point, the oil redeposition varied insignificantly with the washing temperature in all three systems on both fabrics. For any washing solution, the polyester fabric had a higher oil redeposition than that of the cotton fabric at any given washing temperature, reflecting that the hydrophobic oil will attach to the hydrophobic surface of the polyester. Interestingly, the oil redeposition in the DI water system was much higher than those of the two surfactants (the selected formulation and the commercial detergent). Thus, the use of a surfactant not only enhanced the oil detachment but also reduced its redeposition.

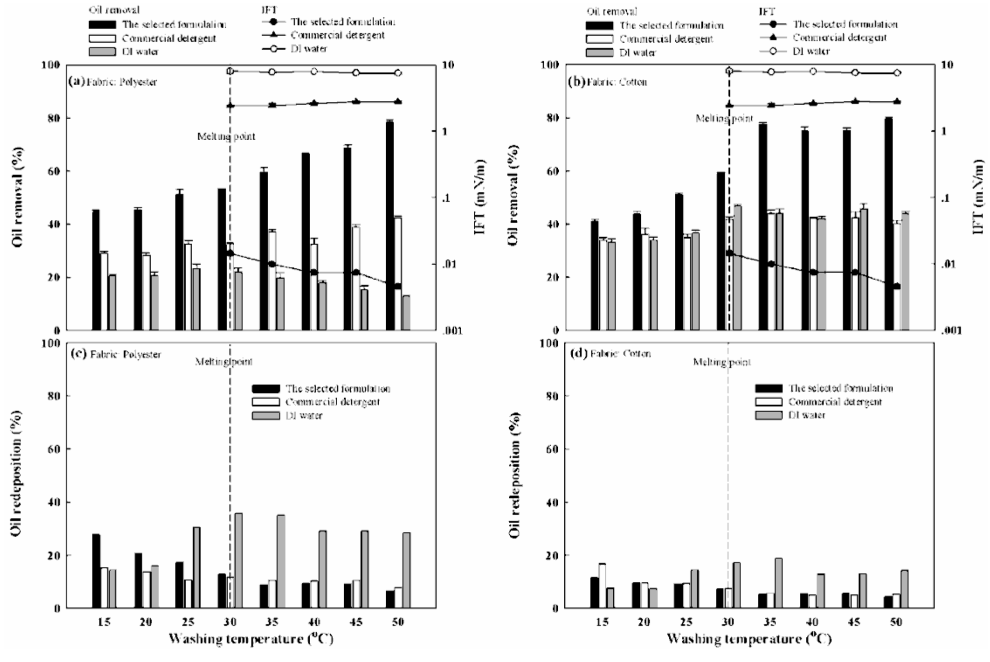

Figure 6.9 Oil removal and redeposition as a function of the washing temperature on the polyester and cotton fabrics in relation to the dynamic IFT using the selected formulation at 0.35 wt% and 5.3 wt% NaCl, in comparison to DI water and the commercial detergent.

6.4.6 Oil Solubilization Results

The proportion of solubilized and unsolubilization (dispersion) oil after a 20 min washing step with 0.35 wt% selected formulation and 5.3 wt% NaCl at different washing temperatures for the cotton and polyester fabrics is shown in **Fig. 10.** For any washing temperature, most of removed oil was found to be as either emulsified liquid droplets or dispersed solid particles with a very small fraction of solubilized oil in micelles, while the solubilized portion slightly increased with increasing washing temperature up to a maximum at 40 °C. At a washing temperature below the oil's melting point, the dispersed oil or unsolubilized portion values was much higher than that at washing temperatures above the melting point. Considering the detergency performance (**Fig. 6.10a** and **6.10b**), comparing the dispersion and solubilization of the removed oil portion, the detergency efficiency appeared to depend on the dispersion stability of the detached oil for both the solidified and liquefied oils.

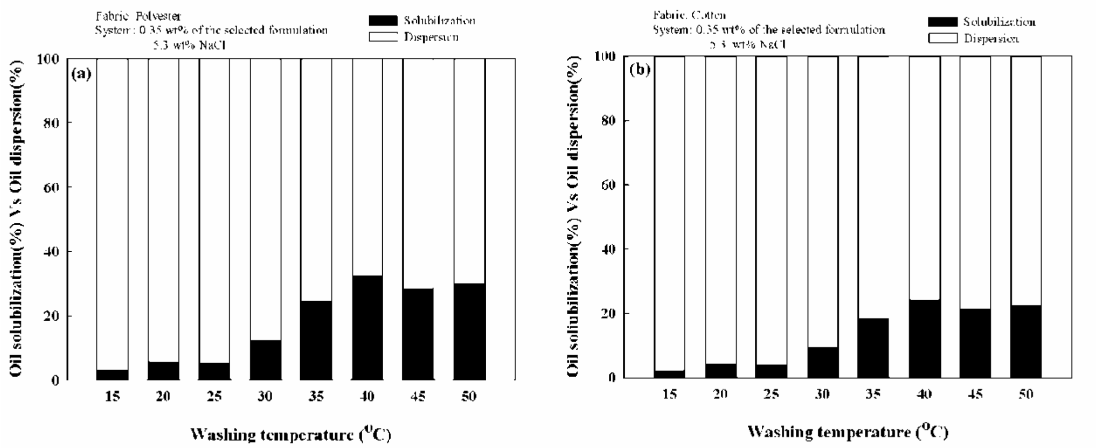

Figure 6.10 Solubilized and unsolubilized portions of the removed oil at 20 min in 0.35 wt% of the selected formulation and 5.3 wt% NaCl as a function of the washing temperature on the (a) polyester and (b) cotton fabrics.

6.4.7 Particle Size Distribution Results

Since most of detached methyl palmitate was in an unsolubilizied form, with solid methyl palmitate particles suspended in the washing solution after the wash step, then their particle size distribution could be ascertained, and that for the detached methyl palmitate particles in the selected formulation, commercial detergent and DI water at different washing temperatures below the melting point are summarized in **Table 6.1**. In all three solutions, the particle sizes of the solidified oil dispersed in the washing solutions had three particle size ranges of low (1–5 μm), medium (5–100 μm) and high (100–600 μm). Increasing the temperature had no significant effect on the particle size distribution or the mean size of the detached methyl palmitate soil particles. The detached methyl palmitate particles in DI water were much larger within the large (100–600 μm) size range and had the largest mean particle sizes compared to those of the two surfactant solutions (the selected formulation and commercial detergent) at any washing temperature on both fabrics. This is because surfactant adsorption onto the detached methyl palmitate particles prevented particle agglomeration. Interestingly, the use of the selected formulation provided the smallest particle sizes of detached methyl palmitate at any washing temperature on both studied fabrics. Presumably the surfactant solution penetrated the methyl palmitate oil by wetting, and so the soil was then dislodged as small particles or droplets causing the apparent correlation between the small particle size and good wettability, leading to a lower oil redeposition and higher oil removal.

Table 6.1 Particle size distribution of methyl palmitate after the washing step from polyester and cotton fabrics using the selected formulation at 0.35 wt% with 5.3 wt% NaCl, in comparison to both DI water and a commercial detergent at different washing temperatures below the melting point

Washing condition	**Cotton**						
	1–5		5–100		100–600		Mean size
	Size	Vol.	Size	Vol.	Size	Vol.	
	(µm)	(%)	(µm)	(%)	(µm)	(%)	(µm)
Washing temperature at 15 °C							
De-ionized water	2.32	9.5	23.4	54.0	267	36.5	110 ±4.3
Commercial detergent	2.39	15.0	18.5	64.0	341	21.0	82.8±4.7
The selected formulation	2.29	21.0	14.9	65.0	356	14.0	60.2±2.1
Washing temperature at 20 °C							
De-ionized water	2.31	9.4	22.2	58.3	281	32.3	104 ±5.6
Commercial detergent	2.26	13.0	22.7	68.5	325	18.5	75.5±5.9
The selected formulation	2.37	20.0	15.9	65.0	306	15.0	55.6±3.4
Washing temperature at 25 °C							
De-ionized water	2.32	9.5	23.2	58.4	282	32.1	101 ±3.9
Commercial detergent	2.28	15.8	18.2	65.9	323	18.3	71.8±9.3
The selected formulation	2.31	16.8	20.0	69.7	237	13.5	49.8±1.9
Washing condition	**Polyester**						
	1–5		5–100		100–600		Mean size
	Size	Vol.	Size	Vol.	Size	Vol.	
	(µm)	(%)	(µm)	(%)	(µm)	(%)	(µm)
Washing temperature at 15 °C							
De-ionized water	3.17	6.4	31.8	52.6	284	41.0	133 ±5.8
Commercial detergent	2.25	11.8	24.0	65.8	345	22.7	93.6±9.1
The selected formulation	2.28	21.0	14.8	65.0	356	14.0	61.5±1.3
Washing temperature at 20 °C							
De-ionized water	3.03	6.5	30.2	57.1	295	36.4	125 ±6.4
Commercial detergent	2.28	14.5	19.0	64.0	349	21.5	87.3±15.5
The selected formulation	2.32	21.5	15.2	63.5	324	15.0	60.3±2.8
Washing temperature at 25 °C							
De-ionized water	2.76	6.50	30.0	57.1	280	36.4	120 ±17.7
Commercial detergent	2.29	14.4	19.5	64.5	355	21.1	87.9±7.7
The selected formulation	2.32	17.9	17.1	66.5	281	15.6	58.4±2.7

6.4.8 Zeta Potential vs. Dispersion Stability

Figure 6.11 shows the correlation between the zeta potential and dispersion stability, in terms of the average absorbance, of methyl palmitate particles in 0.35 wt%of the selected formulation as a function of the salinity at 25 °C. In the absence of NaCl, the magnitude of the zeta potential of methyl palmitate particles was extremely high, due to the ester functional group in methyl palmitate being hydrolyzed into carboxyl and hydroxyl groups, as well as the adsorption of the anionic extended surfactant[7,8,34,35]. The zeta potential of the methyl palmitate particles became less negative with increasing NaCl concentrations, due to the compression of the double layer or reduction of Debye length next to the surface by the co-adsorption of sodium ions from the added NaCl[36,37].

With respect to the dispersion stability, measured in terms of average absorbance, the use of the selected formulation at 0.35 wt% with 5.3 wt% NaCl exhibited the maximum dispersion stability of the methyl palmitate solid particles, which corresponded to the best detergency performance despite the fact that the zeta potential was less negative. For particulate soils, the higher the absolute zeta potential, the higher the electrostatic repulsion, causing a higher the dispersion stability[7,8,31,38]. However, here the zeta potential does not appear to correspond to an increasing dispersion stability or detergency, and so electrostatic interactions are probably not the dominant mechanism for solid non-particulate soil detergency.

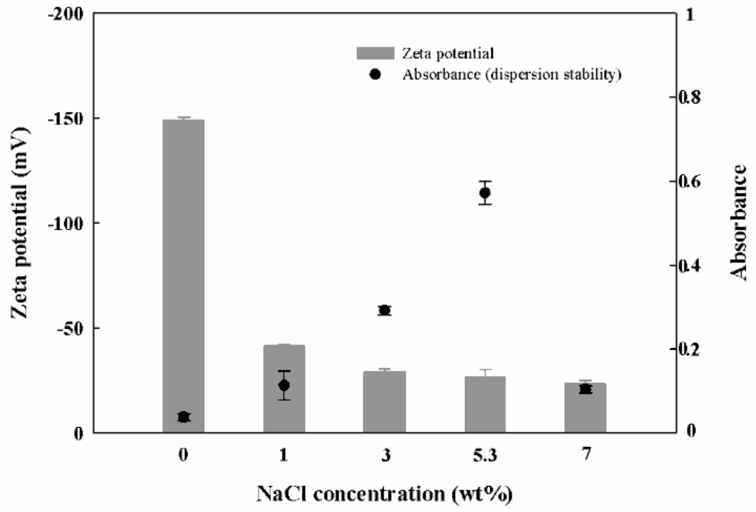

Figure 6.11 The zeta potential and dispersion stability (in terms of the absorbance) of solid methyl palmitate particles as a function of salinity in the selected formulation at 0.35 wt% at 25 °C.

6.4.9 Mechanisms of Solidified and Liquid Oil Detergency

Above the methyl palmitate melting point, the roll up and emulsification of liquid oil with dispersion stability were the dominant mechanism due to the reduction of oil/surfactant solution IFT. The lower the IFT, the higher the oil removal. Below the melting point, the dominant mechanism was the detachment and dispersion stability. The detachment of solidified oil particles from the fabric surface was facilitated by wetting from the surfactant adsorption. The detached solidified oil particles were well dispersed by surfactant adsorption, where the lower the contact angle, the higher oil removal. Both the detached oil droplets and solidified oil particles were then stabilized by surfactant adsorption and most of the detached oil, either in solid or liquid form, was in an insolubilized form.

6.4.10 Conclusion

The selected formulation was able to form a Winsor Type III (middle phase) microemulsion at a high temperature (40 °C), which is above the melting point of methyl palmitate (30 ºC). At temperatures higher than the melting point and under the Winsor Type III microemulsion condition, the maximum oil removal was found to correspond to the minimum system IFT. The selected formulation provided a much higher oily soil detergency compared to that with the commercial detergent or DI water system at any given washing temperature, and most of the detached methyl palmitate was in an unsolubilizied form at washing temperatures lower or higher than the melting point. In comparison with our previous paper, the use of the selected formulation (microemulsion-based) at washing temperatures both below and above the methyl palmitate's melting point gave higher detergency efficiency, especially below the melting point for the polyester around 10-15%, indicating that the microemulsion-based formulation should be employed for detergency application for oil removal in the wide range of washing temperature. According to both results, the removal of liquefied oil resulted from the mechanisms of both roll up, emulsification and dispersion stability while the removal mechanism of the solidified oil was governed the detachment and dispersion stability of solid particles. For oily soil detergency, the system IFT was the most important process parameter in which the lower the IFT, the higher the oil removal. For a non-particulate or waxy soil detergency, the wettability, expressed in terms of the contact angle, was the most important process parameter, where the lower the contact angle, the higher the detergency performance. The use of the microemulsion-based formulation to provide an ultralow IFT for maximum oily detergency also gave a relatively high waxy oil removal.

6.5 Acknowledgments

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CHAPTER VII
CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In Chapter IV, shows the relationships between the removal mechanism of solid fat soil below and above the soil melting point. Above the melting point, lower IFT results in better detergency with varying temperature or salinity, so both solubilization and roll-up are important mechanism. Below the melting point, the detachment of soil as solid particles and dispersion of the particles are the dominant mechanisms of cleaning. Surfactant and salinity improves wetting, dispersion stability, and decreases detached paricles size. Unlike pariculate soil, electrostatics are not the primary driving force for detergency. So, the removal of solid fat soil (Waxy solids) from fabric is fundamentally different from particulate soil.

In Chapter V, six different surfactants were used in this work are alcohol ethoxylate (EO9), sodium dodecyl sulfate (SDS), methyl ester sulfonate (MES), methyl ester ethoxylate (MEE), and two extended surfactants ($C_{12,14}$-10PO-2EO-SO_4Na and $C_{12,14}$-16PO-2EO-SO_4Na). The alcohol ethoxylate (EO9) gave the highest detergency efficiency (at 20 ºC in which the oil is in the solid form) of 75 and 55 % for polyester and cotton, respectively. Interestingly, EO9 shows the highest detergency efficiency at any washing temperature especially on the polyester fabric with the detergency efficiency in the range of 73 to 94 %. The contact angles of all studied surfactants on the methyl palmitate surface were found to well correlate to the detergency performance. The results suggest that the removal of methyl palmitate in a liquidified oil (above its melting point) results from the mechanisms of both roll up and solubilization while the oil removal mechanism of solidified methyl palmitate is governed by the detachment ability by both mechanical force and surfactant adsorption and dispersion stability of detached solidified oil particles.

In Chapter VI, A selected formulation of an anionic extended surfactant (a branched alkyl polypropoxylated sulfate, $C_{12,13}$-4PO-SO_4Na) and sodium mono- and dimethyl naphthalene sulfonate (SMDNS) as a hydrophilic linker was able to form a middle phase microemulsion at a minimum of total surfactant concentration of 0.015 wt% with a weight ratio of $C_{12,13}$-4PO-SO_4Na:SMDNS = 1:0.1625. At a temperature higher than the melting point of methyl palmitate (30°C) and under the Winsor Type III microemulsion condition, the maximum oil removal was found to correspond to the minimum system IFT. The studied formulation provided a much higher oily soil detergency as compared to both commercial and de-ionized water systems. For any temperature below the melting point, on any studied fabrics, the oil removal was significantly lower than that of any system at a temperature higher than the melting point and it decreased with decreasing washing temperature. Under the studied formulation, the solubilization capacity increased with increasing temperature especially at high temperatures whereas the dispersion of detached oil was extremely high and decreased greatly with increasing temperature. The results suggest that the removal of methyl palmitate under liquefied oil results from the mechanisms of both roll up and solubilization while the oil removal mechanism of solidified oils is governed the detachment and dispersion stability of solid particles.

Many studies and researches proposed roll up, emulsification, and solubilization mechanisms of oily soil removal from fabrics as a dominant mechanism. According to the results of this work found that most of the detached methyl palmitate is unsolubilizied form on both washing temperatures as a solid particles or liquid droplets. Therefore, a new proposed mechanism of solid non-particulate soil detergency is the dispersion of detached oil particles in washing solution beginning with the contact angle of surfactant solution onto a flat solid non-particulate soil surface leading to the reduction of surface tension between solid non-particulate soil and surfactant solution. According to the results, the surfactant solution is better able to penetrate into inter-particle clusters and crevices leading to most of the dislodged solid oil particles suspended in the wash solution by repulsive force between charged particles of the adsorbed surfactant molecules.

7.2 Recommendations

There are many things that can leave stains on clothes such as coffee, tea, juice, makeup, chocolate, grease, human sebum skin, clay, and so on. These stains are complex compound which some have both liquid and solid state, so mixed soils between oily soil and particulate soil should be used to imitate as a practical stain dirtied on clothes. Mixed surfactants between anionic and nonionic should be studied to improve detergent formulation because the commercial detergent that used in our daily life has both surfactant types. The washing time that used in detergency experiment should be studied for improving the solid non-particulate soil detergency due to the results of previous works that the washing time was too short for effective oil solubilization. Therefore, improving oil solubilization capacity, soaking step before doing detergency experiment should be focused on.

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APPENDICES

Appendix A Zeta Potential Values at 25 °C

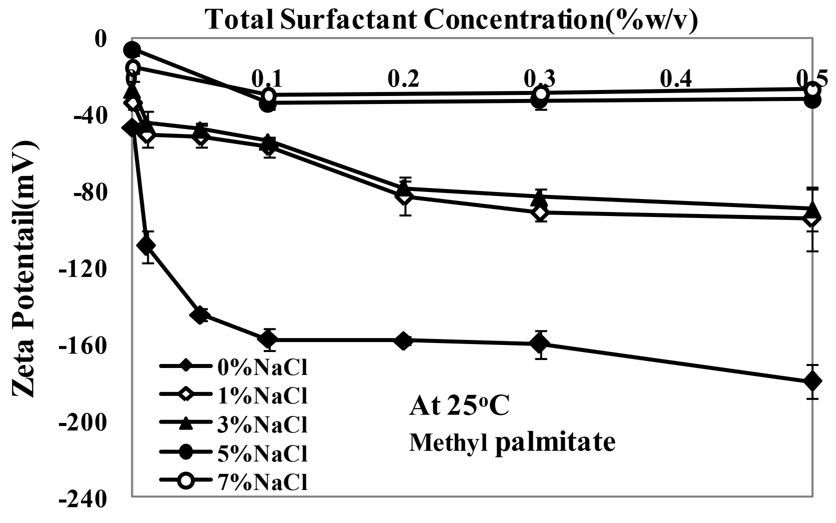

Figure A1 Zeta potential values of methyl palmitate as a function of surfactant and NaCl concentrations.

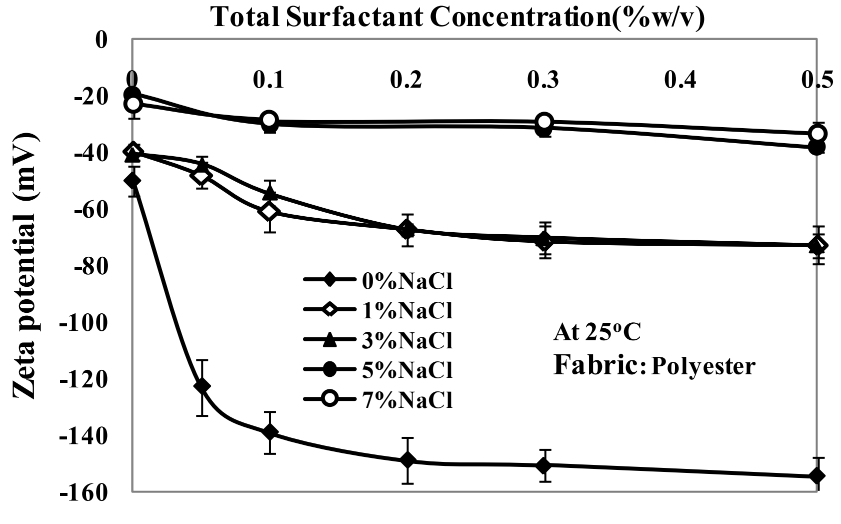

Figure A2 Zeta potential values of polyester as a function of surfactant and NaCl concentrations.

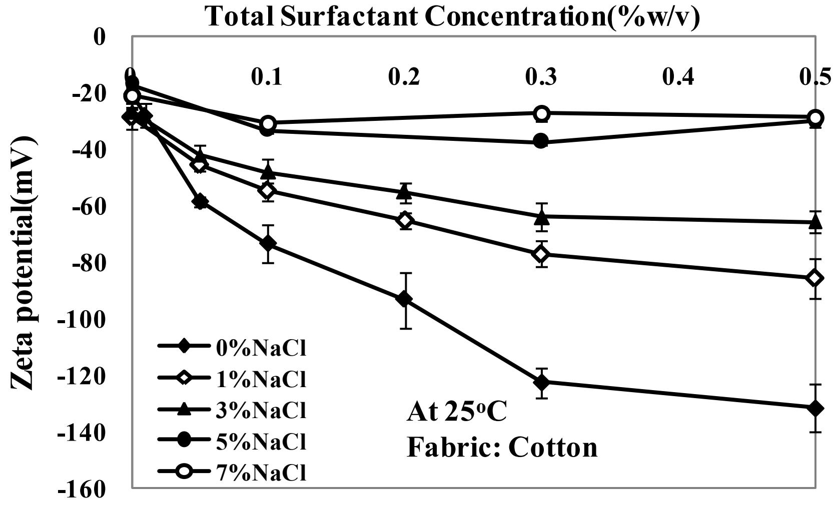

Figure A3 Zeta potential values of cotton as a function of surfactant and NaCl concentrations.

Appendix B The Surface Tension of Extended Surfactant

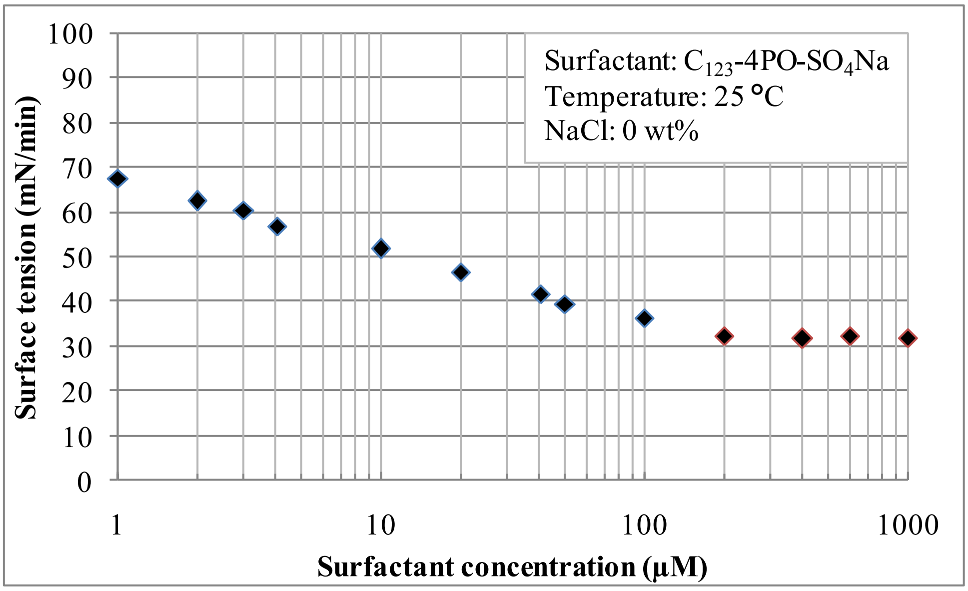

Figure B1 The surface tension of C_{123}-4PO-SO_4Na without NaCl as a function of surfactant concentration at 25 °C.

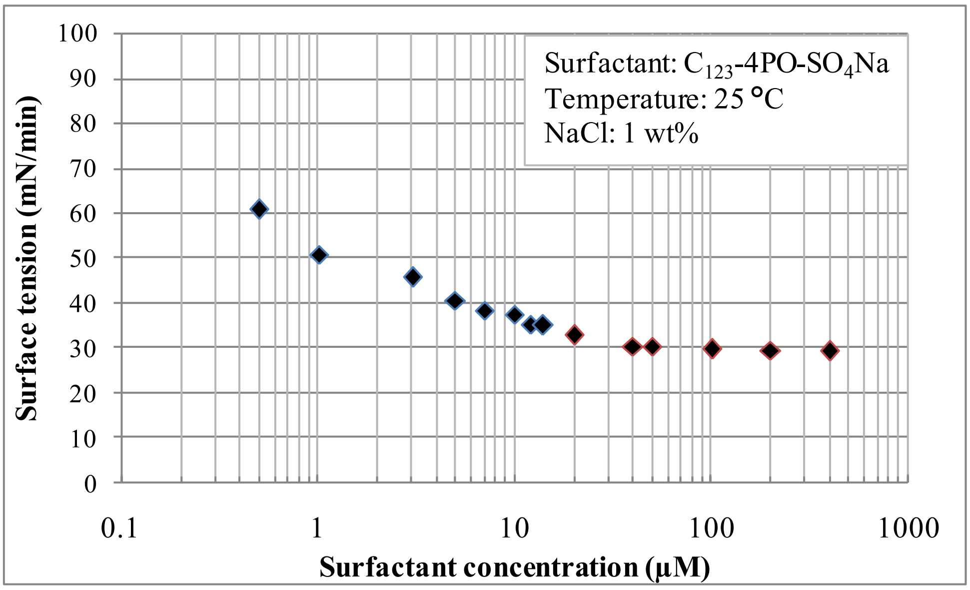

Figure B2 The surface tension of C_{123}-4PO-SO_4Na with 1 wt% NaCl as a function of surfactant concentration at 25 °C.

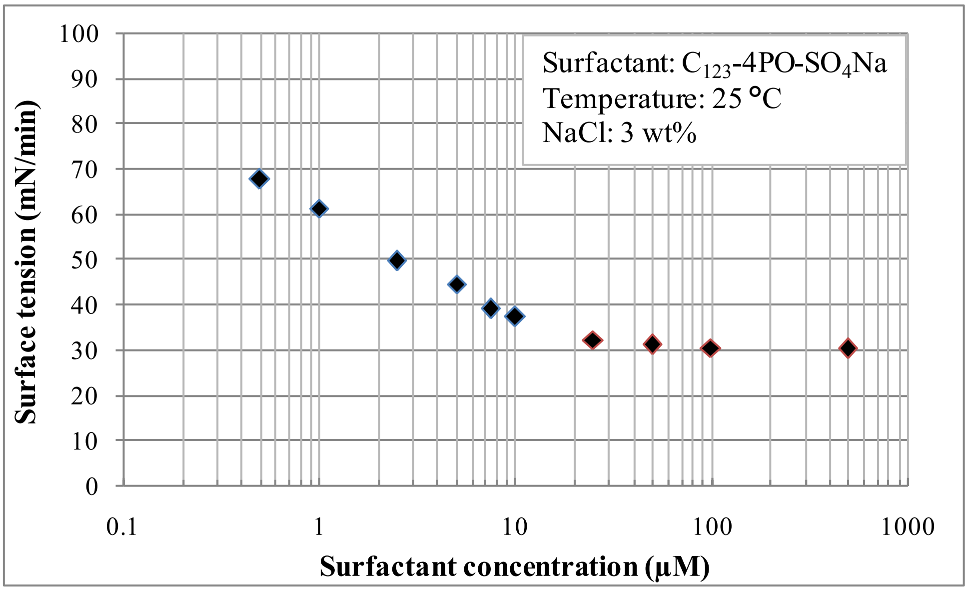

Figure B3 The surface tension of C_{123}-4PO-SO_4Na with 3 wt% NaCl as a function of surfactant concentration at 25 °C.

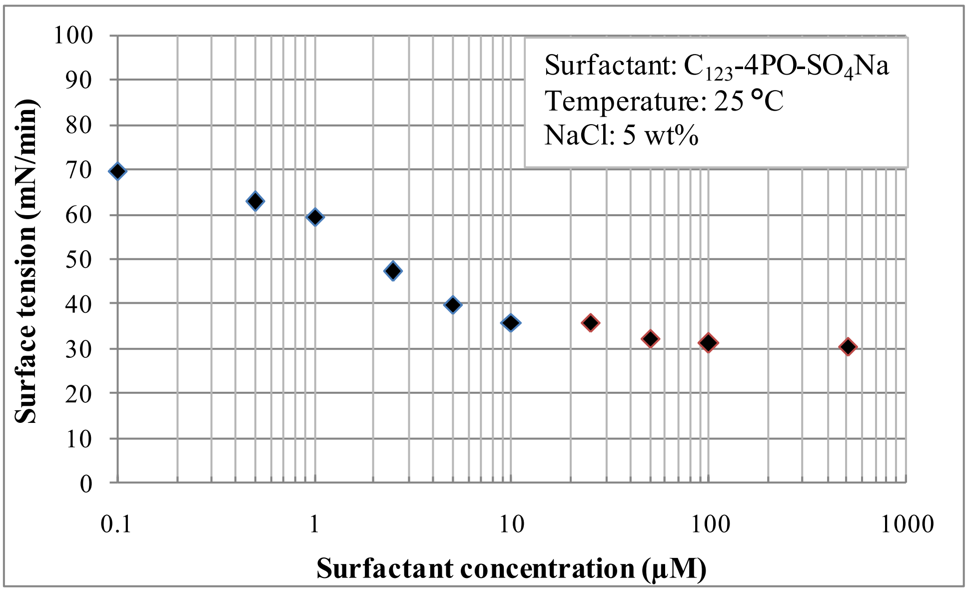

Figure B4 The surface tension of C_{123}-4PO-SO_4Na with 5 wt% NaCl as a function of surfactant concentration at 25 °C.

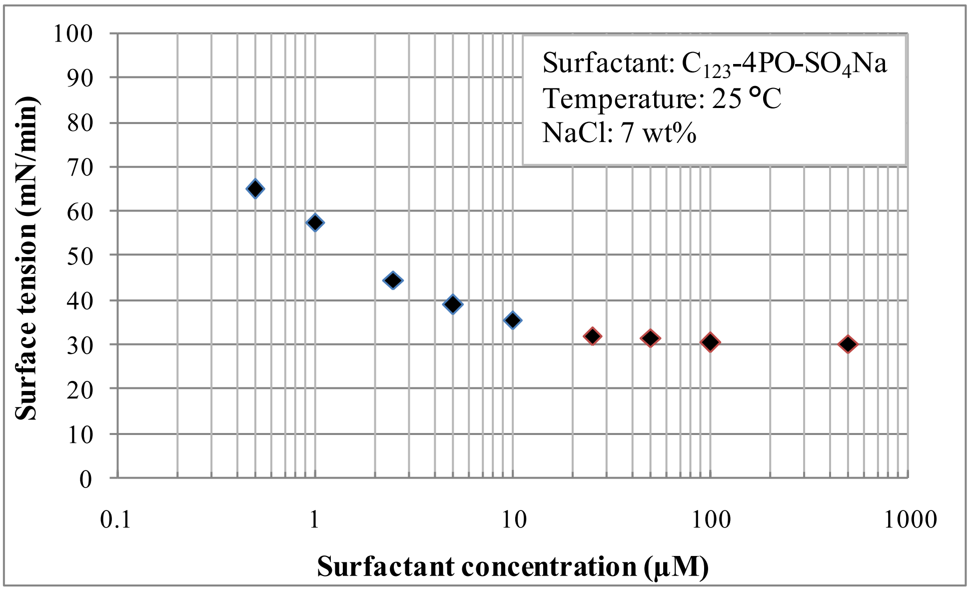

Figure B5 The surface tension of C_{123}-4PO-SO_4Na with 7 wt% NaCl as a function of surfactant concentration at 25 °C.

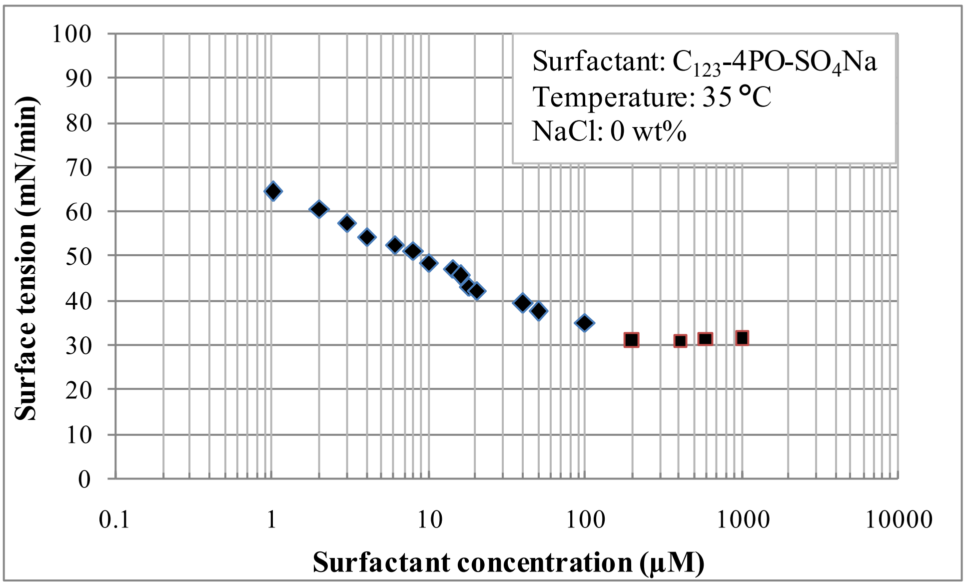

Figure B6 The surface tension of C_{123}-4PO-SO_4Na without NaCl as a function of surfactant concentration at 35 °C.

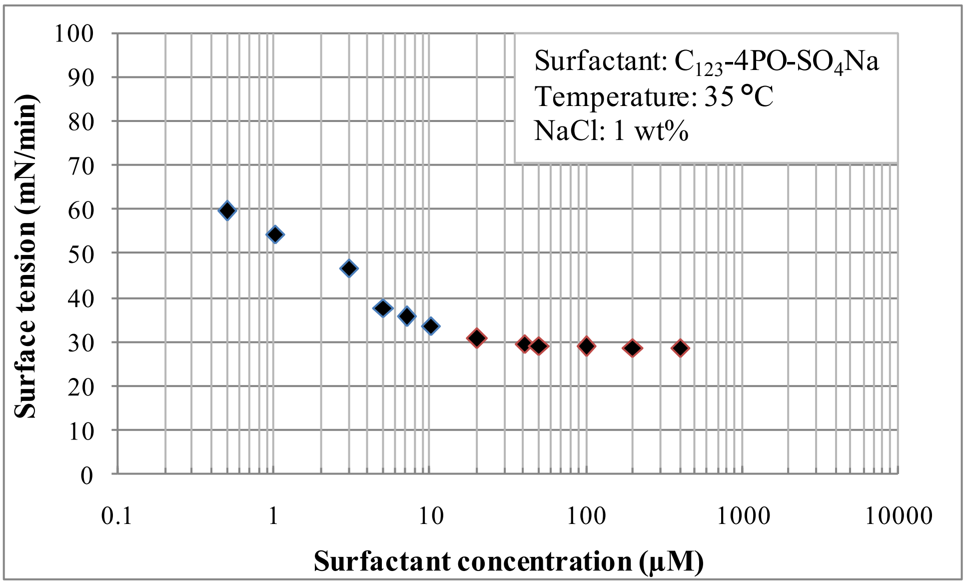

Figure B7 The surface tension of C_{123}-4PO-SO_4Na with 1 wt% NaCl as a function of surfactant concentration at 35 °C.

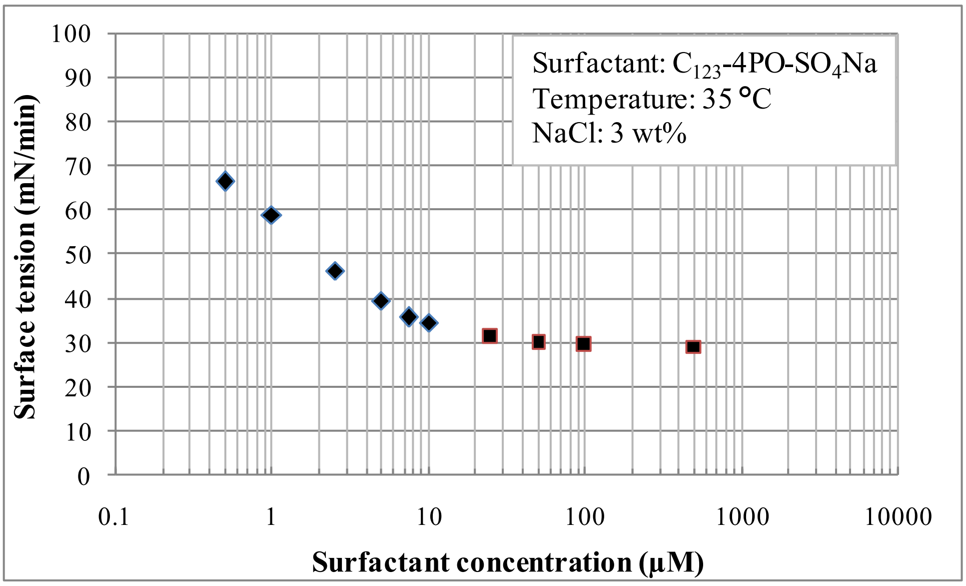

Figure B8 The surface tension of C_{123}-4PO-SO_4Na with 3 wt% NaCl as a function of surfactant concentration at 35 °C.

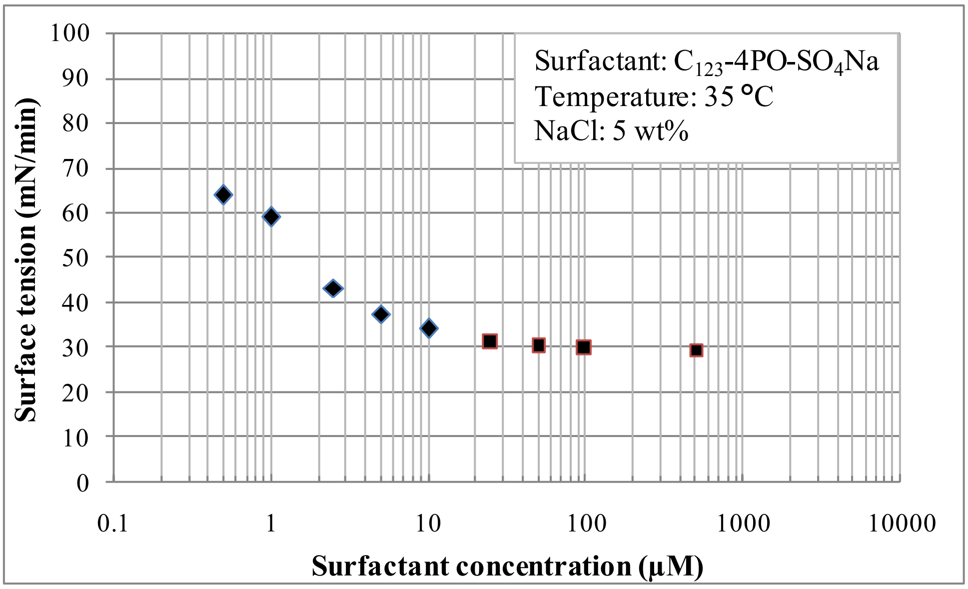

Figure B9 The surface tension of C_{123}-4PO-SO_4Na with 5 wt% NaCl as a function of surfactant concentration at 35 °C.

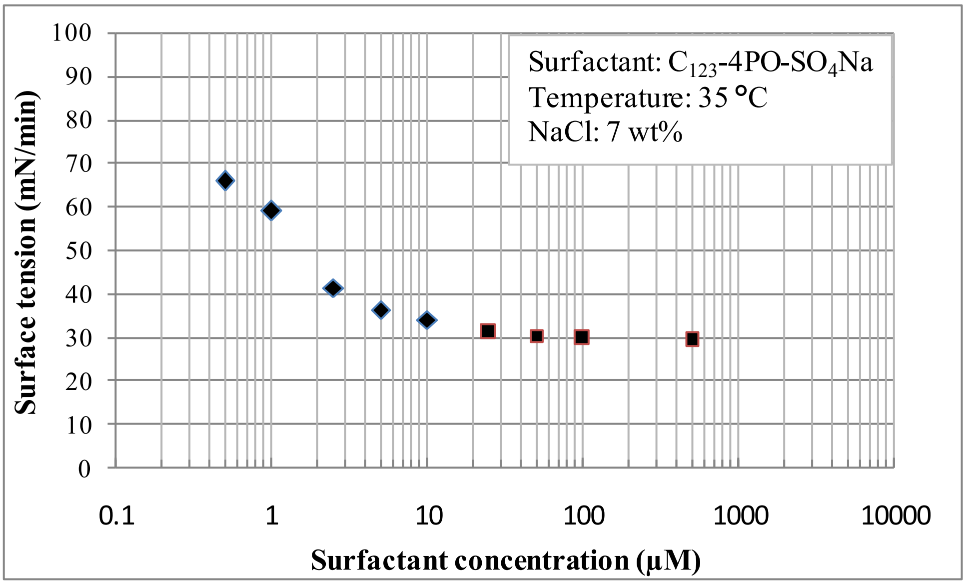

Figure B10 The surface tension of C_{123}-4PO-SO_4Na with 7 wt% NaCl as a function of surfactant concentration at 35 °C.

Appendix C Dynamic Interfacial Tension (IFT)

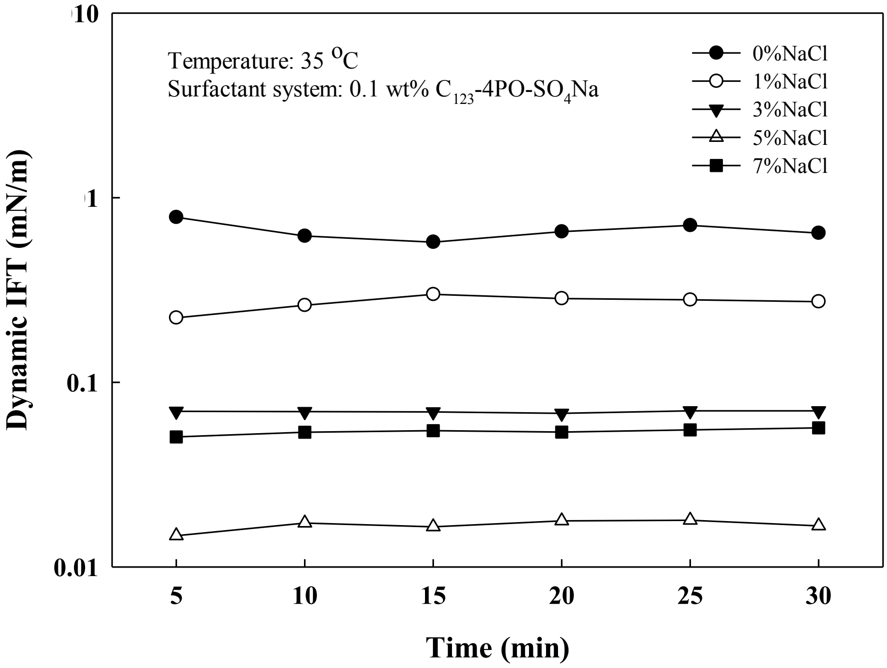

Figure C1 The dynamic interfacial tension of C_{123}-4PO-SO_4Na as a function of time at 35 °C.

Appendix D Particle Size Distribution

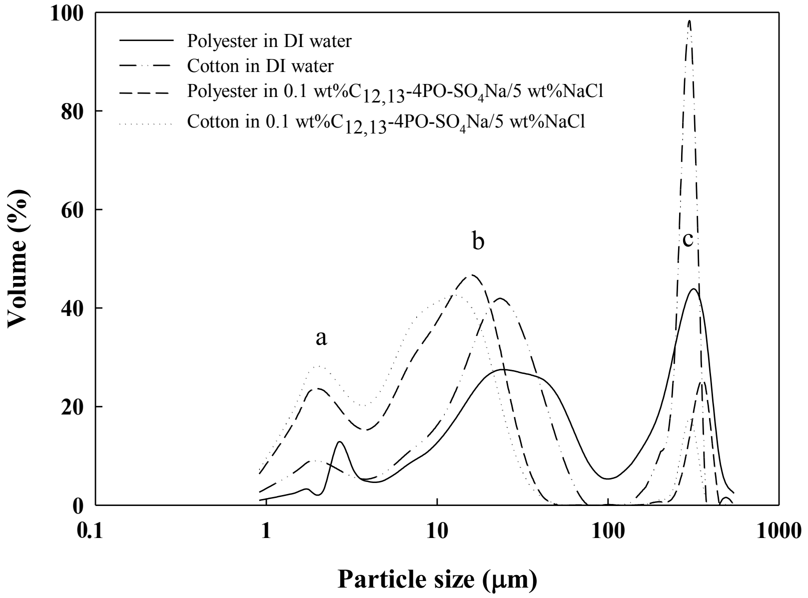

Figure D1 The particle size distribution of methyl palmitate after washing step with C123-4PO-SO4Na and DI water solution at 25 °C; (a) 1-5 μm, (b) 5-100 μm, and (c) 100-600 μm.

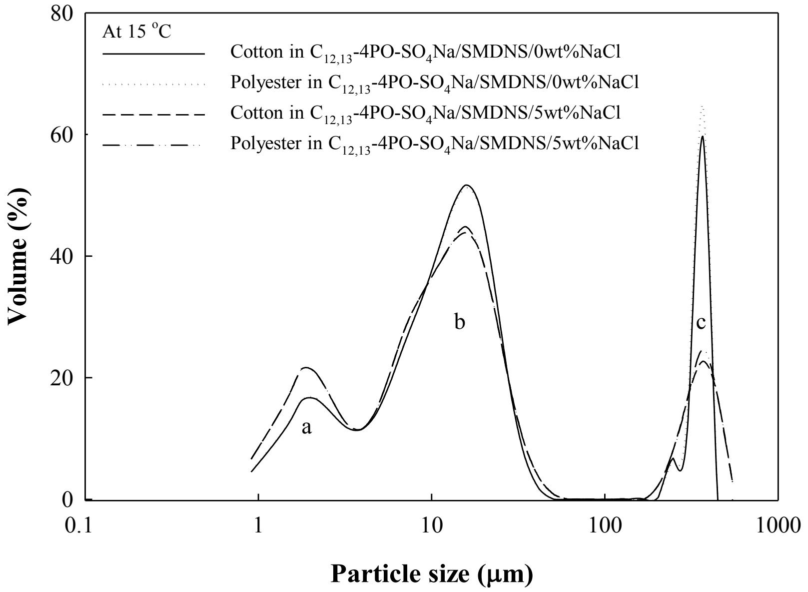

Figure D2 The particle size distribution of methyl palmitate after washing step with C123-4PO-SO4Na/SMDNS at 15 °C; (a) 1-5 μm, (b) 5-100 μm, and (c) 100-600 μm.

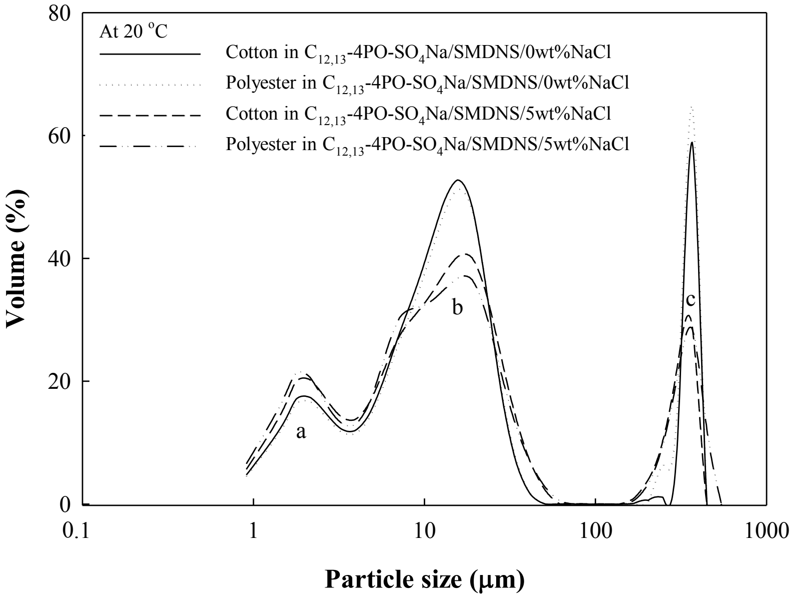

Figure D3 The particle size distribution of methyl palmitate after washing step with C123-4PO-SO4Na/SMDNS at 20 °C; (a) 1-5 µm, (b) 5-100 µm, and (c) 100-600 µm.

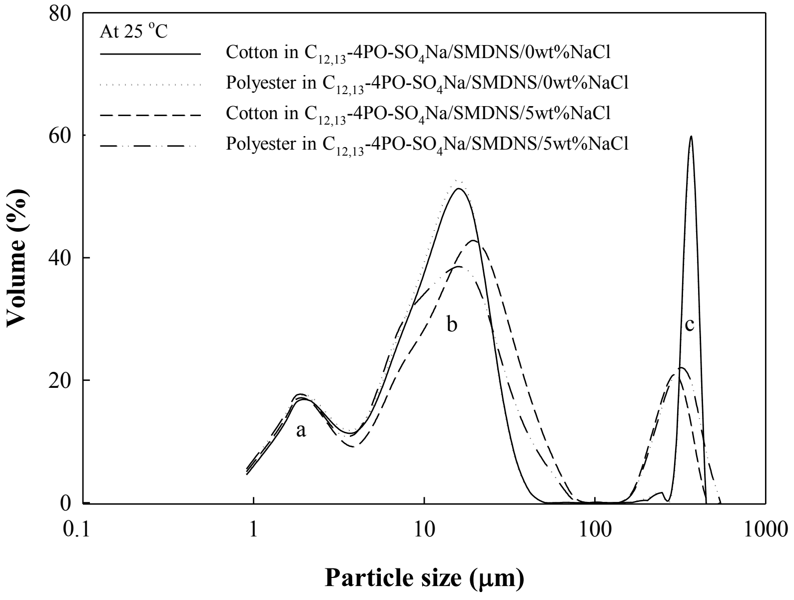

Figure D4 The particle size distribution of methyl palmitate after washing step with C123-4PO-SO4Na/SMDNS at 25 °C; (a) 1-5 µm, (b) 5-100 µm, and (c) 100-600 µm.

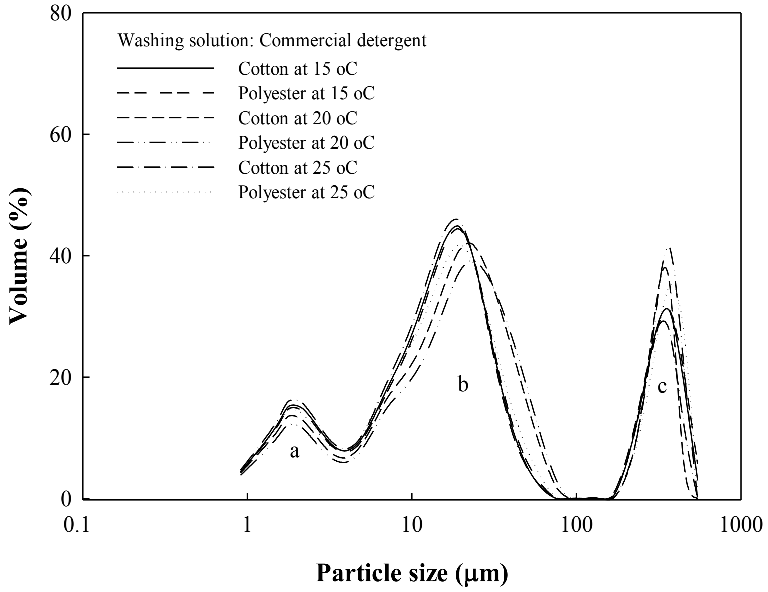

Figure D5 The particle size distribution of methyl palmitate after washing step with commercial product at different washing temperature; (a) 1-5 μm, (b) 5-100 μm, and (c) 100-600 μm.

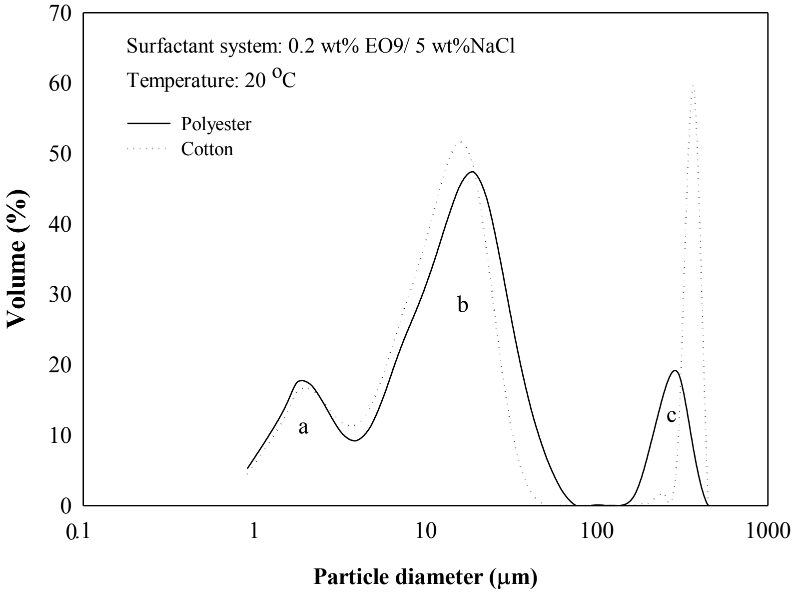

Figure D6 The particle size distribution of methyl palmitate after washing step with EO9 with 5 wt% NaCl at 20 °C; (a) 1-5 μm, (b) 5-100 μm, and (c) 100-600 μm.

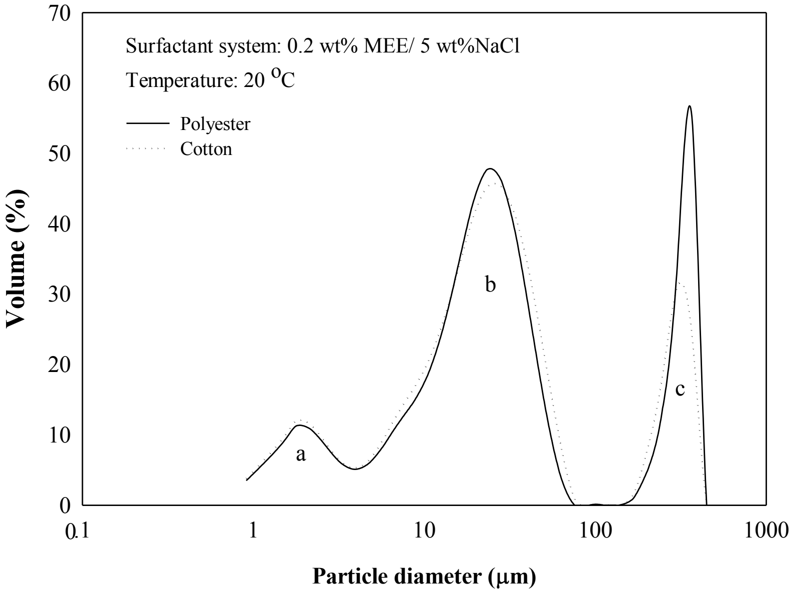

Figure D7 The particle size distribution of methyl palmitate after washing step with MEE with 5 wt% NaCl at 20 °C; (a) 1-5 μm, (b) 5-100 μm, and (c) 100-600 μm.

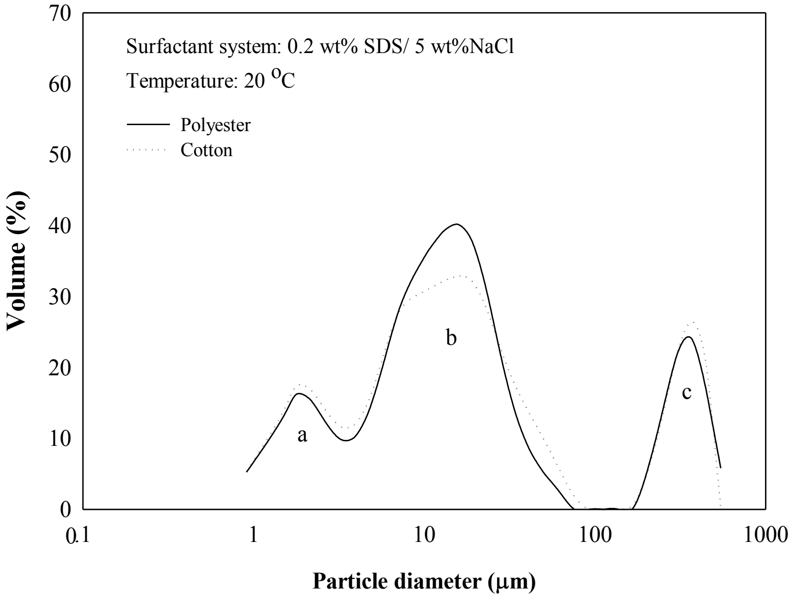

Figure D8 The particle size distribution of methyl palmitate after washing step with SDS with 5 wt% NaCl at 20 °C; (a) 1-5 μm, (b) 5-100 μm, and (c) 100-600 μm.

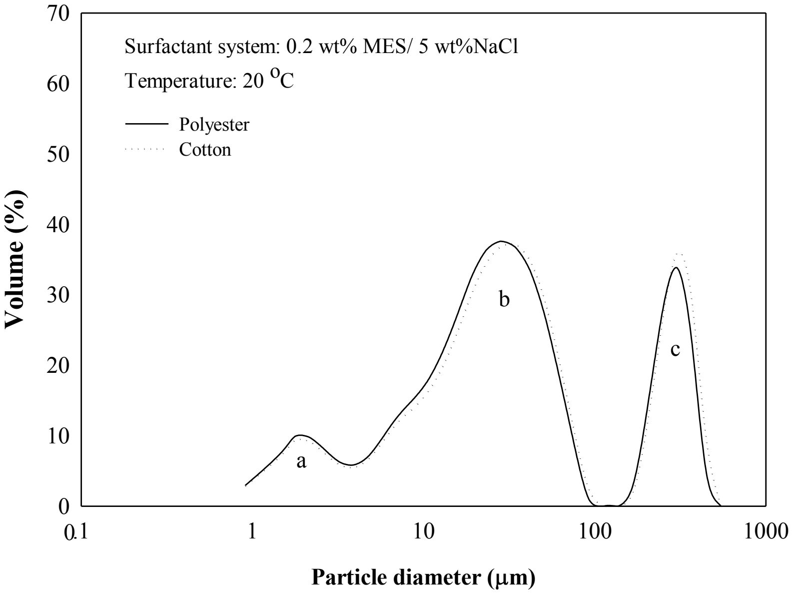

Figure D9 The particle size distribution of methyl palmitate after washing step with MES with 5 wt% NaCl at 20 °C; (a) 1-5 μm, (b) 5-100 μm, and (c) 100-600 μm.

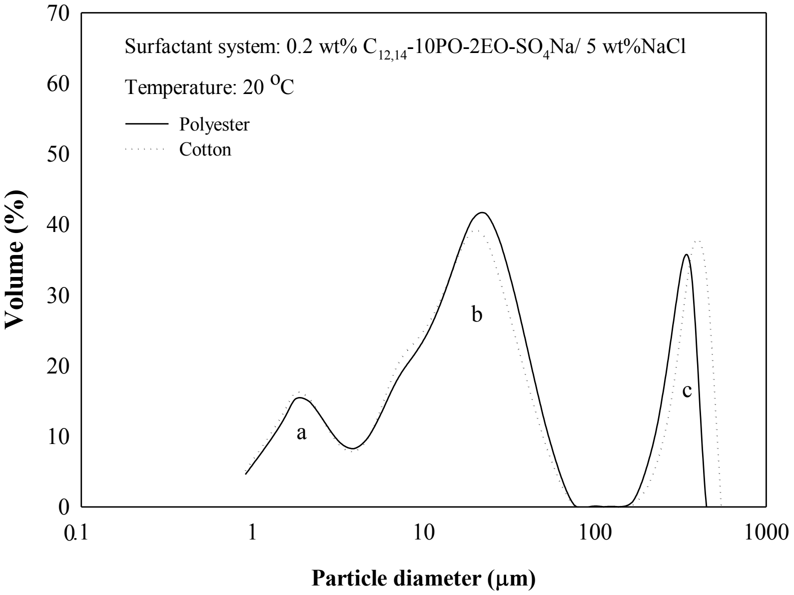

Figure D10 The particle size distribution of methyl palmitate after washing step with $C_{12,14}$-10PO-2EO-SO_4Na with 5 wt% NaCl at 20 °C; (a) 1-5 μm, (b) 5-100 μm, and (c) 100-600 μm.

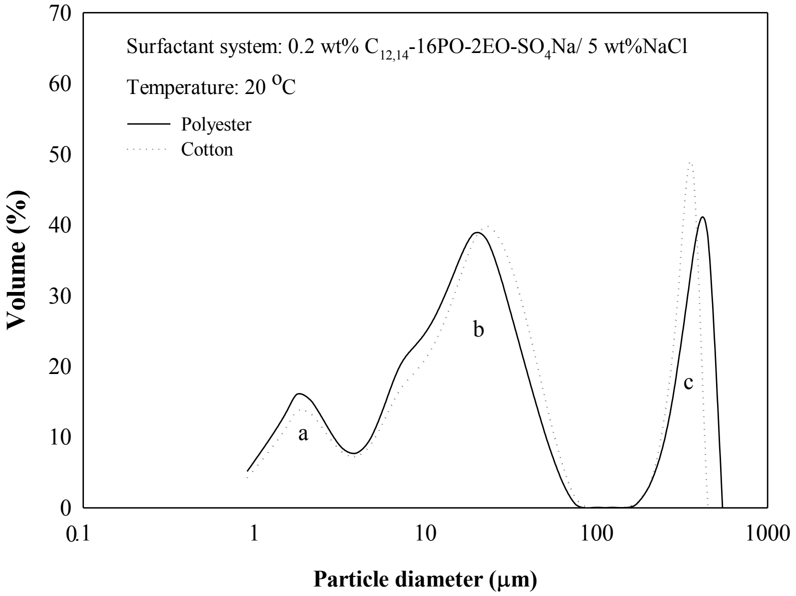

Figure D11 The particle size distribution of methyl palmitate after washing step with $C_{12,14}$-16PO-2EO-SO_4Na with 5 wt% NaCl at 20 °C; (a) 1-5 μm, (b) 5-100 μm, and (c) 100-600 μm.

Appendix E Scanning Electron Microscope (SEM) Images

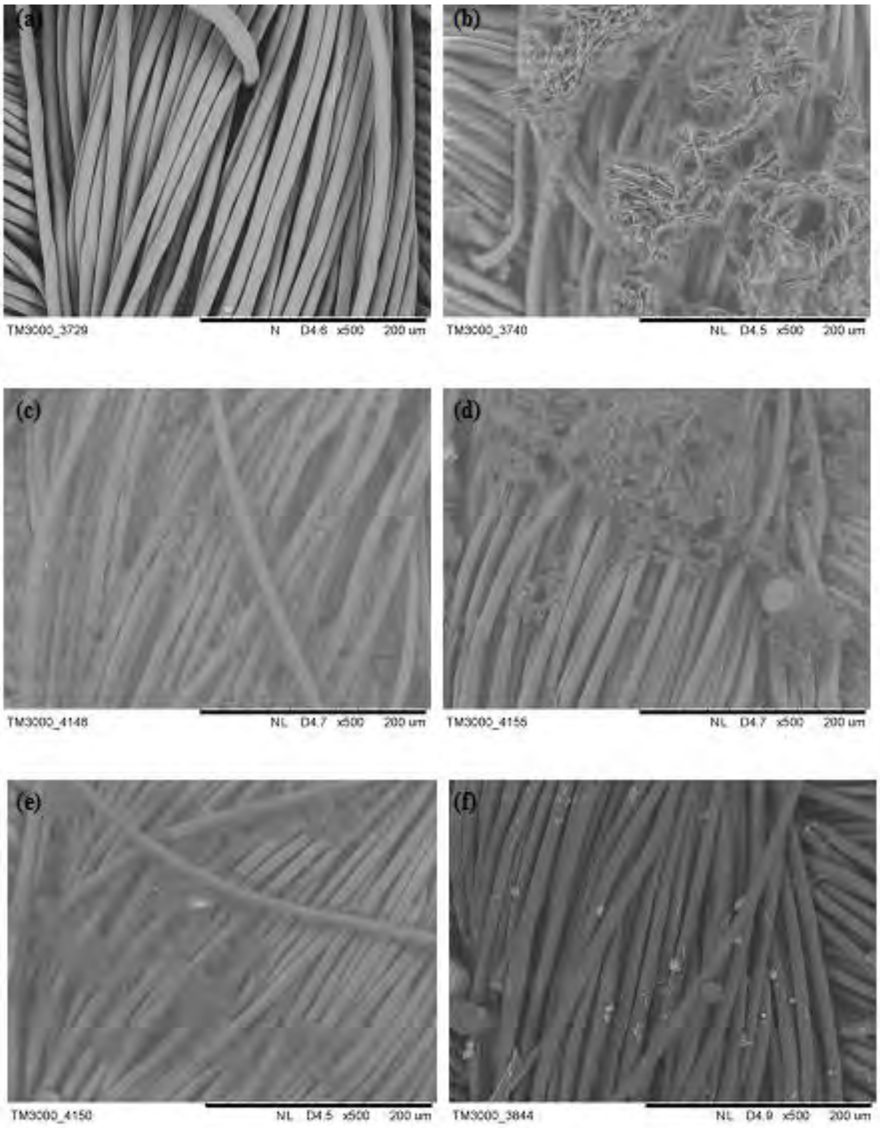

Figure E1 SEM micrograph of polyester fabrics (×500); (a) before soiling, (b) after soiling with methyl palmitate, (c) after washing with DI water at 20°C, (d) after washing with DI water at 40°C, (e) after washing with 0.1 wt% $C_{12,13}(PO)_4SO_4$ and 5 wt% NaCl at 20°C, and (f) after washing with 0.1 wt% $C_{12,13}(PO)_4SO_4$ and 5 wt% NaCl at 40°C.

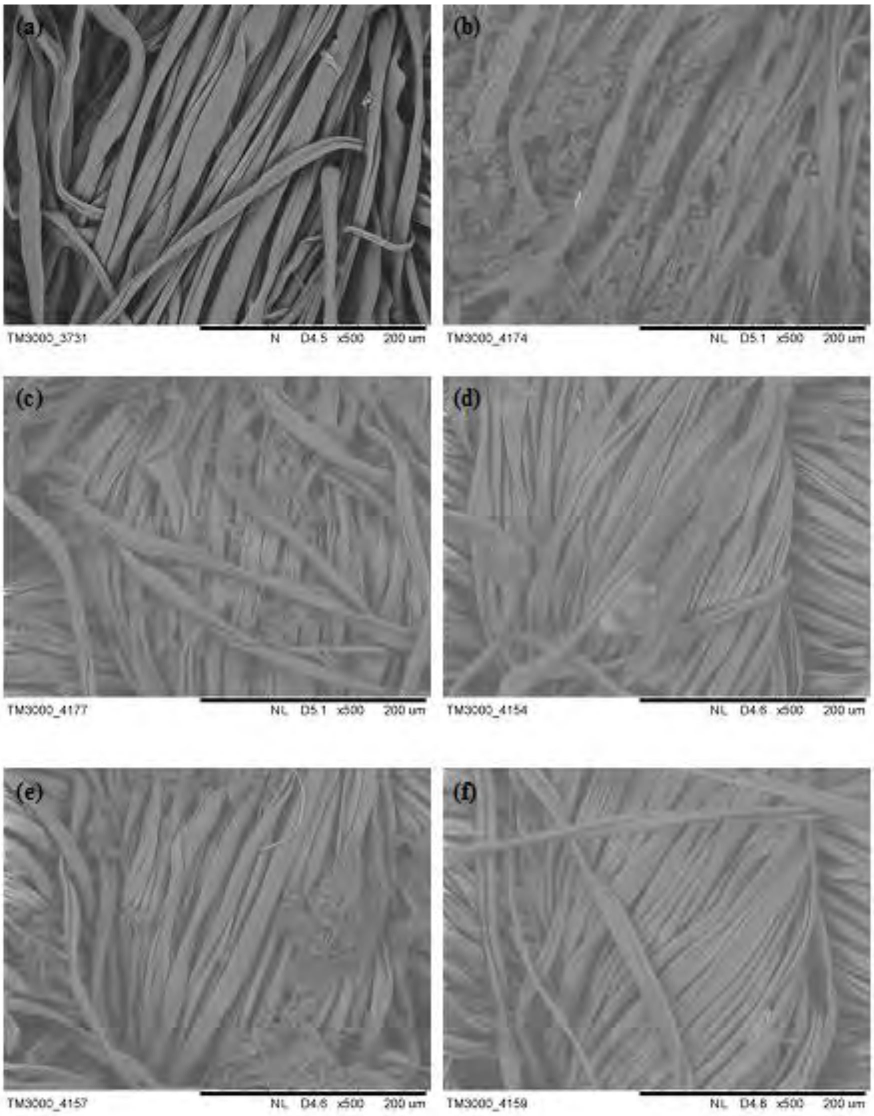

Figure E2 SEM micrograph of cotton fabrics (×500); (a) before soiling, (b) after soiling with methyl palmitate, (c) after washing with DI water at 20°C, (d) after washing with DI water at 40°C, (e) after washing with 0.1 wt% $C_{12,13}(PO)_4SO_4$ and 5 wt% NaCl at 20°C, and (f) after washing with 0.1 wt% $C_{12,13}(PO)_4SO_4$ and 5 wt% NaCl at 40°C.

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1. Chanwattanakit, J.; Scamehorn, JF.; Sabatini, DA.; and Chavadej, S. (2017) Laundry Detergency of Solid Non–Particulate Soil or Waxy Solids: Part I. Relation to Oily Soil Removal Above the Melting Point. Journal of Surfactants and Detergents, 20, 815-830.
2. Chanwattanakit, J.; Scamehorn, JF.; Sabatini, DA.; and Chavadej, S. (2017) Laundry Detergency of Solid Non–Particulate Soil or Waxy Solids: Part II. Effect of Surfactant Types. Journal of Surfactants and Detergents, in preparation.
3. Chanwattanakit, J.; and Chavadej, S. (2017) Laundry Detergency of Solid Non–Particulate Soil Using Microemulsion-Based Formulation. Journal of Oleo Science, review in process.

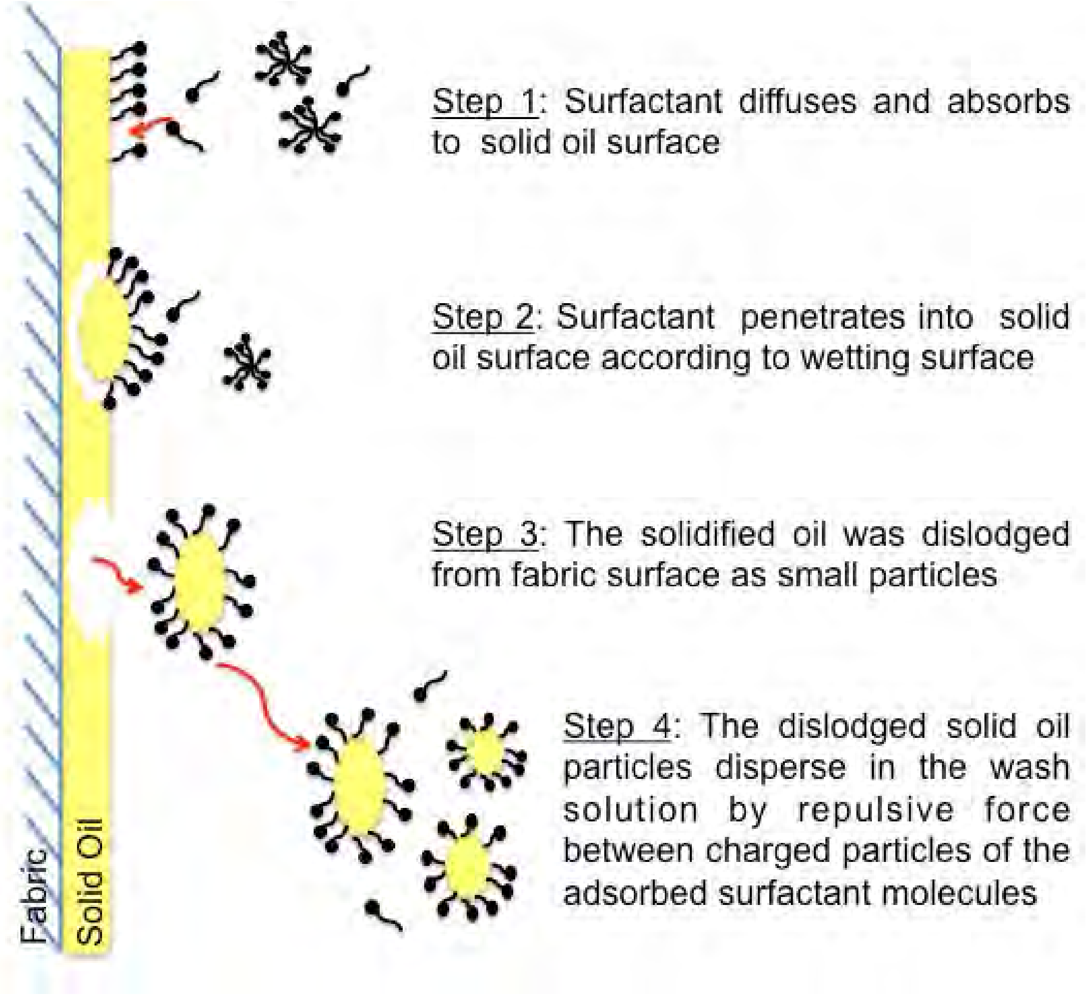
Presentation:

1. Chanwattanakit, J.; Scamehorn, JF.; Sabatini, DA.; and Chavadej, S. (2012, April 29—May 2) Solid Oily Soil Removal from Fabrics by Using Extended Surfactants. Oral presentation at The 103rd AOCS Annual Meeting & Expo 2012, Long Beach, California, USA.
2. Chanwattanakit, J.; Scamehorn, JF.; Sabatini, DA.; and Chavadej, S. (2012, September 30— October 4) Solid Monoglyceride(fat) soil Removal from Fabrics. Poster presentation atThe World Congress on Oleo Science & 29th ISF Congress (WCOS2012), Arkas Sasebo, Nagasaki, Japan.
3. Chanwattanakit, J.; Scamehorn, JF.; Sabatini, DA.; and Chavadej, S. (2013, April 28—May 1) Monoglyceride Removal from Fabrics under Microemulsion-Based Formulation. Oral presentation at The 104th AOCS Annual Meeting & Expo 2013, Montréal, Québec, Canada.

4. Scamehorn, JF.; Chanwattanakit, J.; and Chavadej, S. (2013, June 10—12) Detergency with Solid Non-Particulate Soil (Waxy Solid) –A Critical Chanllenge in Cold-Water Detergency. Oral presentation at 9th World Surfactant Congress and Business Convention, Barcelona, Spain.
5. Chanwattanakit, J.; Scamehorn, JF.; Sabatini, DA.; and Chavadej, S. (2015, 31 August – 4 September) Mechanisms and Performance of Methyl Palmitate (Solid Fat Soil) Detergency under Microemulsion-Besed Formulation. Poster presentation at European Conference on Surface Science (ECOSS-31), Barcelona, Spain.
6. Chanwattanakit, J.; Scamehorn, JF.; Sabatini, DA.; and Chavadej, S. (2015, November 24-27) Solid Fat Soil Detergency By Using Various Surfactant Systems. Oral presentation at 6th Asian Conference on Colloid and Interface Science, Arkas Sasebo, Sasebo, Japan.
7. Chanwattanakit, J.; Scamehorn, JF.; Sabatini, DA.; and Chavadej, S. (2016, June 19–22) Mechanisms of Oily Soil Detergency: Relation to Liquid and Solid States of Oil. Poster presentation at 6th International Colloids Conference, Berlin, Germany.
8. Sabatini, DA.; Scamehorn, JF.; Chanwattanakit, J.; and Chavadej, S. (2017, April 30–May 3) Laundry Detergency of Solid Non-Particulate Soil or Waxy Solids: Relation to Oily Soil Removal Above the Melting Point. Oral presentation at 2017 AOCS Annual Meeting and Industry Showcases, Orlando, Florida, USA.

Graphical Abstract

Mechanism and Performance of Solid Non-Particulate Soil (Waxy Solid) Removal From Fabrics



Step 1: Surfactant diffuses and absorbs to solid oil surface

Step 2: Surfactant penetrates into solid oil surface according to wetting surface

Step 3: The solidified oil was dislodged from fabric surface as small particles

Step 4: The dislodged solid oil particles disperse in the wash solution by repulsive force between charged particles of the adsorbed surfactant molecules

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ORIGINAL ARTICLE

Laundry Detergency of Solid Non-particulate Soil or Waxy Solids: Part I. Relation to Oily Soil Removal Above the Melting Point

Jarussri Chanwattanakit[1] · **John F. Scamehorn**[2] · **David A. Sabatini**[2] · **Sumaeth Chavadej**[1,3]

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Abstract In this work, methyl palmitate or palmitic acid methyl ester, a monoglyceride, was used as both a model solid fat below the melting point and as an oily soil above the melting point. An anionic extended surfactant [branched alcohol propoxylate sulfate sodium salt (C_{123}-$(PO)_4$-SO_4Na)] was used to remove methyl palmitate from cotton and from polyester. Above the melting point (~30 °C) of methyl palmitate, the maximum oily soil removal was found to correspond to the lowest dynamic interfacial tension, as is common with liquid soils. Below the melting point, the lower the contact angle of the wash solution against the soil (indicating higher wettability), the higher the solid fat soil detergency. The removed methyl palmitate was found to be mostly in unsolubilized droplets or particles with a small fraction of micellar solubilization for both solid and liquid forms. The presence of surfactant can prevent the agglomeration of detached methyl palmitate particles in both liquid and solid forms, reducing redeposition and enhancing detergency. Below the melting point, the surfactant aids the solution wetting the surfaces, then penetrating the waxy solid, causing detachment as small particles, and dispersion of these particles. Unlike particulate soil detergency, electrostatic forces are not the dominant factor in fatty soil detergency.

Keywords Solid non-particulate soil · Solid fat soil · Methyl palmitate · Extended surfactant · Laundry detergency

Introduction

In laundry detergency, several factors affect the performance such as the nature of soils, the properties of surfactant, nature of solid surface, mechanical action applied during washing, water hardness, washing temperature, electrolyte level, and additives (e.g., builder, enzyme, and anti-redeposition agent) [1–5]. The previous work on oily soil detergency using different liquid oils demonstrated good correlation between detergency efficiency and interfacial tension (IFT) between the oil and the aqueous solution [6–13]. Recently, our research group has published studies of the mechanisms of particulate soil detergency using carbon black as a model hydrophobic soil and kaolinite and ferric oxide as model hydrophilic soils. It was found that electrostatic forces dominate soil removal, even for nonionic surfactants and hydrophobic fabric [14, 15].

Solid non-particulate soil or solid fat soil is a separate class of contaminants which has properties of liquid and/or solid, depending on temperature. Practical examples of such soils are butter, sebum from human skin, or solidified hamburger or bacon grease. These soils are particularly challenging to remove in low temperature laundry detergency, which is a current topic of great interest due to energy savings and fabric damage at high temperatures. Often, soils are mixtures between liquid and solid fat soils in which the liquid oil is entrapped in the crystal structure of solid oil under a moderate temperature, causing it to be hard to remove. Despite the importance of this soil removal in practical detergency, there are few literature studies of

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solid fat soil detergency. Scheuing [16] studied the detergency mechanism of tristearin (model solid fat soil) using Fourier transform infrared spectroscopy (FT-IR) and reported that the removal of solid triglycerides from a fabric surface was more complex than solid hydrocarbon soils because of the polymorphism in the crystal structure of tristearin. Powe [17] studied detergency of different hydrocarbon soils, and found that the maximum removal of each solid fat soil was somewhere near its melting point. Kawase *et al*. [18, 19] studied the removal mechanism of solid fatty acid soil by using nonionic and anionic surfactants and they reported that solubilization was the dominant mechanism at low temperatures.

An extended surfactant has a group of intermediate polarity, such as polypropylene oxide (PO) or polypropylene–polyethylene oxide (PO–EO) group, inserted between the hydrophilic head and hydrocarbon tail group. As a result of this unique structure, extended surfactants can further extend into both the oil and aqueous phases, resulting in a smoother transition between the hydrophobic and hydrophilic regions at the interface. The presence of a polypropylene oxide group in the hydrocarbon tail of the surfactant molecule helps extend the tail to an oil phase, while still maintaining good interaction with the water phase. Hence, use of an extended surfactant can facilitate the formation of a middle-phase microemulsion, which provides both high solubilization and ultralow interfacial tension (IFT), leading to various applications such as extraction, separation, and textile cleaning [20–23]. Phan *et al*. [24] examined the use of a single extended surfactant in detergency of vegetable oils. High canola oil detergency (>80%) was achieved using a single extended surfactant ($C_{14,15}$-8PO-SO_4Na) at concentrations as low as 125 ppm and a temperature of 25 °C. Tanthakit *et al.* [8] studied palm oil removal from fabric using microemulsion-based formulations of a mixture of an extended surfactant ($C_{14,15}$-3PO-SO_4Na) and a nonionic secondary alcohol ethoxylated surfactant [$C_{12,14}$-O(EO)$_5$] at a 25:75 weight ratio. The oil removal for this surfactant blend exceeded 90%, which was greater than those of any single surfactant alone and of a commercial liquid laundry detergent. Do *et al.* [25] reported that the mixture of a linear extended surfactant (C_{10}-18PO-2EO-SO_4Na) and a hydrophobic twin-tailed sodium dioctylsulfosuccinate surfactant showed synergism in a Winsor Type III microemulsion formulation, leading to high detergency of vegetable oils and semi-solid fats at low salinity and a low washing temperature.

In this paper, methyl palmitate or palmitic acid methyl ester, a monoglyceride, with a melting point around 30 °C, was used as a model single component solid fat or oily soil being removed from either hydrophilic surface (cotton fabric) or hydrophobic surface (polyester fabric) by using a single anionic extended surfactant at temperatures both higher and lower than the soil's melting point. Other fundamental physical properties of the system were studied to better understand the forces involved in soil removal and help guide future development of cold water detergent formulations.

Experimental Procedures

Materials

Methyl palmitate or palmitic acid methyl ester (99.8% purity) and Oil red O (solvent Red 27, No. 26125) were supplied by Sigma-Aldrich (BKK, Thailand). Cotton and polyester were purchased from Test fabrics, Inc. (Middlesex, NJ, USA). The surfactant used in this study was an extended surfactant which is a branched alcohol propoxylate sulfate sodium salt with 12–13 carbon numbers with approximately four propylene oxide (PO) units ($C_{12,13}$-4PO-SO_4Na) with an active content of 30 wt%, as provided by Sasol North America (Lake Charles, LA). Sodium chloride (NaCl), dichloromethane, and isopropanol, all analytical grade, were purchased from LabScan Asia Co., Ltd. De-ionized (DI) water was used to prepare all solutions.

Fabric Pretreatment and Soiling Procedure

Pre-washing of the test fabrics was done using de-ionized (DI) water to eliminate all residues of mill-finishing agents. The pre-washing method followed the ASTM standard guide D4265-98 [26]. After pre-washing, the fabric was cut into 3 × 4 inch swatches in a warp and weft direction. Approximately 0.1 g of the oil-soluble dye was added to 100 mL of the oil above its melting point. The colored oil was filtered until clear. Next, 10 mL of the clear dyed oil was diluted with dichloromethane to 100 mL [27]. The swatches were folded and completely submerged in the diluted dyed oil solution for 5 min. The soiled fabrics were then unfolded and laid on a flat glass plate in a ventilated hood at room temperature (25 °C) overnight in order to dry the soiled swatches. All swatches were freshly prepared for each batch of laundry experiments. By this soiling method, the average weight ratios of oil-to-fabric were approximately 0.20 ± 0.01:1 for the cotton and 0.15 ± 0.01:1 for the polyester.

Laundry Experiments

The laundry experiments were conducted using a terg-o-tometer (Copley, DIS 8000), which simulates a home washing-machine action in a bench scale unit. The experimental procedure consisted of a wash step for 20 min with

1000 mL of a surfactant washing solution and two rinse steps for 2 and 3 min with 1000 mL of DI water. An agitation speed for each step was fixed at 120 rpm. Three soiled swatches and one unsoiled swatch for anti-redeposition testing were washed in each bucket for one cycle for replication.

Oil Removal Measurement

Oil removal was quantified based on residual oil on the swatches after washing. The residual oil was extracted by submerging a swatch in isopropanol for 24 h at room temperature, and then the extracted solution was analyzed by an ultraviolet/visible spectrophotometer (Hewlett-Packard, 8452A) [9, 27]. The oil removal was calculated by subtracting the remaining oil residue after washing from the original oil content in each swatch.

Surface Tension Measurements

The surface tension of a surfactant solution with varying surfactant and NaCl concentrations was measured by a Wilhelmy plate tensiometer (Krüss, K100) at two different temperatures (25 and 35 °C). The inflection point of the plot of surface tension versus the log of initial surfactant concentration was used to determine the critical micelle concentration (CMC) [28].

Particle Size Measurement

The particle size distribution of methyl palmitate particles suspended in the washing solution after the wash step at 20 °C was measured by a particle size analyzer (Malvern, Mastersizer X).

Contact Angle Measurement

A 2-μL drop of a surfactant solution with different NaCl concentrations and two surfactant concentrations of 0.1 and 0.3 wt% was placed on the methyl palmitate surface by using a micro-syringe and the contact angle was measured after 30 s by a contact angle measuring instrument (Krüss, DSA 10 Mk2) using the sessile drop technique. During the measurement, the sample chamber was kept at 25 °C in order to prevent melting of the sample (methyl palmitate).

Oil Solubilization Measurement

An excess amount of methyl palmitate was added to a surfactant solution having a surfactant concentration of 1000 mg/L (10 times CMC) with 5 wt% NaCl or a surfactant concentration of 3000 mg/L (30 times CMC) with 1 or 5 wt% NaCl at different temperatures. The solution was stirred at 120 rpm for 20 min. The surfactant solution phase of the mixture was filtered and the filtrate was measured for total carbon concentration of the dissolved methyl palmitate plus the surfactant by a total organic carbon analyzer (TOC) (Shimadzu, TOC 5000). The TOC concentration of dissolved methyl palmitate was obtained by subtracting the total TOC value with the TOC value of surfactant. The solubility of methyl palmitate obtained was then subtracted from the oil removal to determine the portion of unsolubilized (dispersed or emulsified) methyl palmitate. The measurement time of 20 min was selected to be the same as the wash step time used in the washing experiments. In addition, the oil solubilization measurement was also carried out with varying time until each system reached a maximum or equilibrium solubilization level which was found at around 24 h for all studied systems.

Interfacial Tension Measurement

The measurement of dynamic interfacial tension (IFT) between the aqueous phase (the surfactant solution) and the oil phase (methyl palmitate) for varying surfactant concentrations and temperatures (higher than the melting point of methyl palmitate) was conducted using a spinning drop tensiometer (University of Texas, Model 500). A volume of 1–3 μL of methyl palmitate (above the melting point) was injected into a 300-μL capillary tube filled up with a surfactant solution having different NaCl concentrations and two surfactant concentrations of 0.1 and 0.3 wt%. The diameter of the oil drop was recorded 20 min after injection, which corresponded to the time used for the wash step in detergency experiments.

Dispersion Stability Measurement

The dispersion stability of methyl palmitate solid particles having average diameters of 100 μm suspending in DI water or an aqueous solution containing 0.1 or 0.3 wt% surfactant with different NaCl concentrations at 25 °C (below the melting point) was determined by measuring absorbance as a function of time using a UV–visible spectrophotometer (Hewlett-Packard, 8452A). The solution was prepared by adding the methyl palmitate particles in the surfactant solution, after being well mixed; the prepared solution was transferred to a spectrophotometer cuvette. The reading of absorbance at a wavelength of 550 nm was recorded every 10 s for 2 h. The absorbance values in the range of 2000–5000 s were averaged to represent the dispersion stability. The higher the absorbance, the higher the dispersion stability.

PZC Measurement

A powder sample of methyl palmitate or cotton or polyester fabric was added to distilled water at different solution pH values using a 0.1 M HCl or 0.1 M NaOH solution for pH adjustment. After that, the solution with any added powder sample was kept at 20 °C for 24 h. The initial pH value of this solution, prior to adding the powder sample, and the final pH after 24 h were measured by a pH meter (Ultra basic DENVER Instrument). The point of the intersection of the initial and the final pH lines was used to indicate the point of zero charge (PZC) of each material.

Zeta Potential Measurement

About 3.5 mg of methyl palmitate powder was added into a solution having 0.1 wt% surfactant and different NaCl concentrations. The mixture was stirred and kept at 20 °C for 24 h. Subsequently, the solution was transferred to an electrophoretic cell of a zeta meter (Zeta-Meter 3.0+) equipped with a microscope module. After applying a suitable voltage, the charged particles moved towards the electrode having opposite charge until attaining a steady state (the particles moved with a constant velocity). The velocities were measured and averaged and referred to as electrophoretic mobility which was calculated by the zeta meter instrument automatically [29].

Results and Discussion

Detergency Performance: Optimum Concentrations of Surfactant and NaCl

As shown in Table 1, added surfactant or NaCl has a negligible effect on the melting point of methyl palmitate (we use 30 °C throughout this paper). Figure 1 shows the oil removal and oil redeposition as a function of surfactant concentration and salinity for cotton and polyester at 35 and 25 °C in which methyl palmitate is in a liquid form and solid form, respectively. At 35 °C, for any given NaCl concentration, with increasing surfactant concentration, the oil removal increased and leveled off for both test fabrics. For any given surfactant concentration, the oil removal reaches a maximum at 5 wt% NaCl as shown in Fig. 1a-1, b-1. At 25 °C, the oil removal gradually increases with increasing surfactant concentration and the oil removal reaches a maximum at 1 wt% NaCl as shown in Fig. 1c-1, d-1. In this work, the ability of low extended surfactant concentration to achieve good detergency is consistent with results of previous studies [23, 24].

Table 1 Melting point of methyl palmitate in various washing solutions

Solution	Melting point (°C)
De-ionized water	29.5–30.4
0.1 wt% $C_{12,13}(PO)_4SO_4Na$	28.5–30.1
0.1 wt% $C_{12,13}(PO)_4SO_4Na$/1 wt% NaCl	28.2–30.3
0.1 wt% $C_{12,13}(PO)_4SO_4Na$/3 wt% NaCl	29.5–30.3
0.1 wt% $C_{12,13}(PO)_4SO_4Na$/5 wt% NaCl	28.0–30.4
0.1 wt% $C_{12,13}(PO)_4SO_4Na$/7 wt% NaCl	29.5–30.2

Figure 1 also shows the effects of salinity and surfactant concentration on the oil redeposition on cotton and polyester at 35 and 25 °C. The amount of oil redepositing on both fabrics decreased with increasing surfactant concentration and leveled off at a high surfactant concentration, depending on the concentration of added NaCl. For any fixed surfactant concentration, the oil redeposition reached a minimum value at 5 and 1 wt% NaCl at 35 and 25 °C, respectively. The maximum oil removal with the lowest oil redeposition was found at the same surfactant concentration and salinity for both fabrics types and for both washing temperatures.

CMC Results

The CMC values of the extended surfactant with different NaCl concentrations at 25 and 35 °C are shown in Fig. 2a. Increasing electrolyte NaCl concentration causes the CMC to decrease due to decrease of the absolute value of the electrical potential at the micelle surface and lower electrostatic repulsion between surfactant head groups at the micelle surface [20, 23]. Moreover, the CMC values were relatively independent of temperature (those at 25 °C were slightly higher than those at 35 °C for all NaCl concentrations), consistent with low temperature dependence of CMC on temperature for anionic surfactants [30]. The CMC data from Fig. 2a are plotted as the logarithm of critical micelle concentration versus logarithm of total concentration of counterion in the solution at the CMC (from added NaCl and surfactant) as shown in Fig. 2b. This log–log plot is linear and known as the Corrin–Harkins plot [31]. The absolute value of the slope from these plots is the fractional counterion binding to micelles and at 25 °C is 0.29 and at 35 °C is 0.30. These values are only about half of those measured for other ionic surfactants [32, 33], so extended surfactants show unusual electrostatic properties, probably having to do with the packing of the head groups at the micelle surface. In common with other ionic surfactants, fractional counterion binding on micelles has only slight temperature dependence.

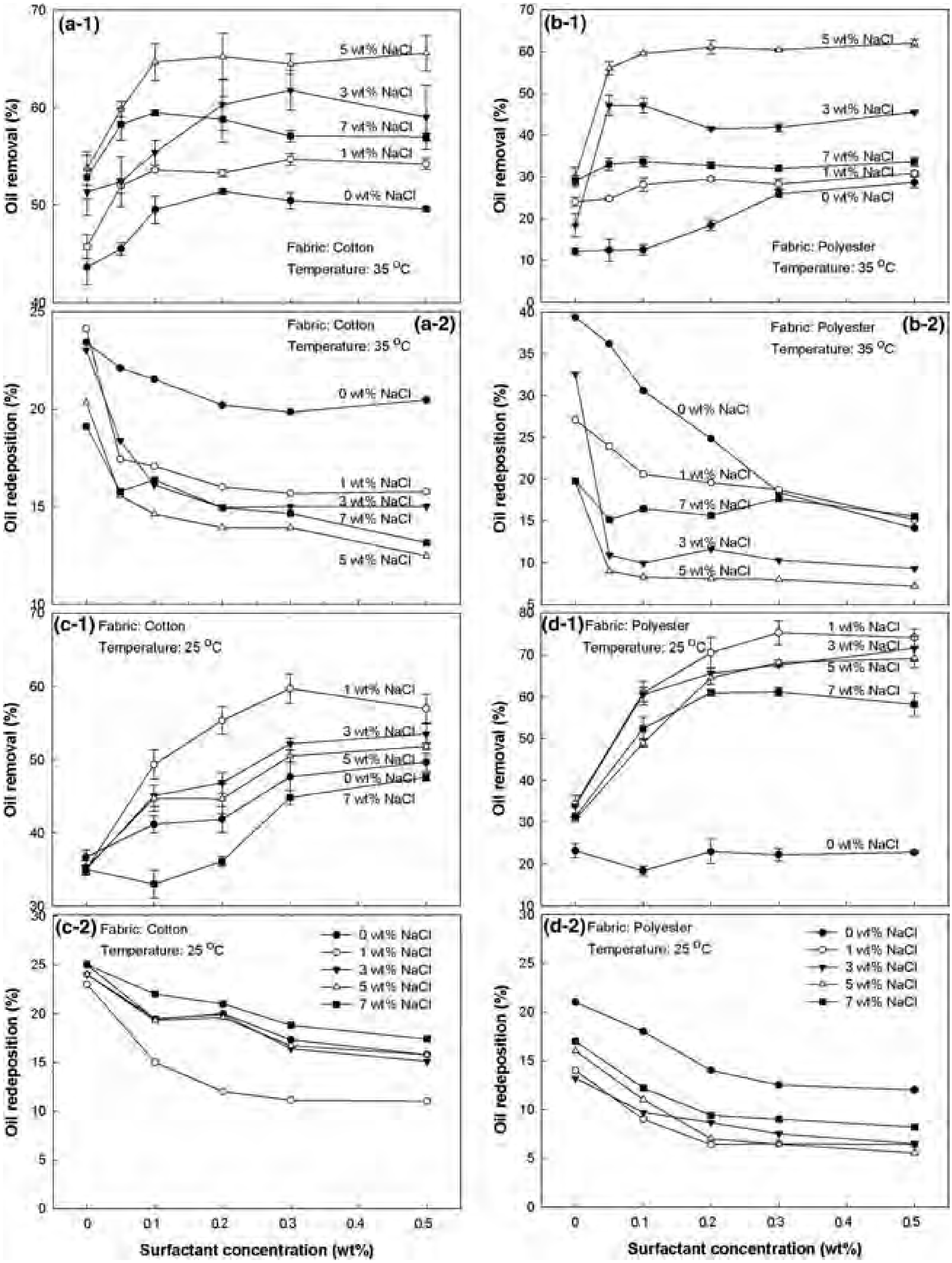

Fig. 1 Oil removal and redeposition of methyl palmitate as a function of surfactant concentration and salinity on both test fabrics **a-1**, **a-2** for cotton at 35 °C, **b-1**, **b-2** for polyester at 35 °C, **c-1**, **c-2** for cotton at 25 °C, **d-1**, **d-2** for polyester at 25 °C

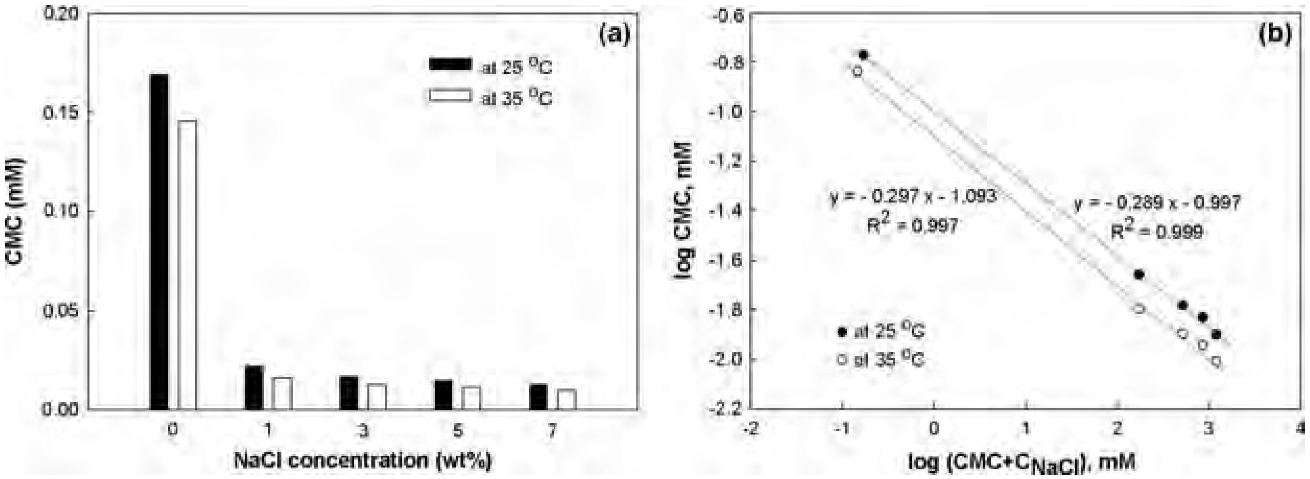

Fig. 2 **a** Critical micelle concentration (CMC) of $C_{12,13}(PO)_4SO_4Na$ at 25 and 35 °C and **b** Corrin and Harkins plot of $C_{12,13}(PO)_4SO_4Na$ from CMC data at 25 and 35 °C

Interfacial Tension (IFT) Results

Figure 3 shows the IFT at the interface of the liquid methyl palmitate and surfactant solution as a function of salinity for two surfactant concentrations of 0.1 and 0.3 wt% at 35°C. The IFT values of the surfactant solution and the liquid oil were measured at 20 min, which is long enough for equilibration [34] and corresponds to the wash step time used in the washing experiments. For both studied surfactant concentrations, all of the surfactant solution–oil IFT values measured (0.0172–0.2773 mN/m) are considered to be in the low and ultralow ranges, except at 0 wt% NaCl (2.39 mN/m) which agree well with the measured IFT values between an extended surfactant and canola oil [24, 34, 35]. All of the measured IFT values were much lower than the deionized water–oil IFT value (7.86 mN/m) and the 5 wt% NaCl deionized water–oil IFT value (7.29 mN/m).

Contact Angle Results

The contact angle is a physical parameter indicative of how well an applied solution wets a surface. The wetting is a first step of the complex process of detergency. Figure 4 shows the contact angles of both 0.1 and 0.3 wt% surfactant solutions on the solid surface of methyl palmitate as a function of NaCl concentration at 25 °C. The contact angle decreases with increasing NaCl concentration and reaches a minimum value (indicating maximum wettability) at a NaCl concentration of 5 and 1 wt% for 0.1 and 0.3 wt% surfactant concentrations, respectively. An increase in surfactant concentration from 0.1 to 0.3 wt% could reduce the optimum NaCl concentration studied for detergency performance from 5 to 1 wt%. This surfactant concentration increase to 0.3 wt% also resulted in a decreased contact angle from 38° to 33° at 5 and 1 wt% NaCl,

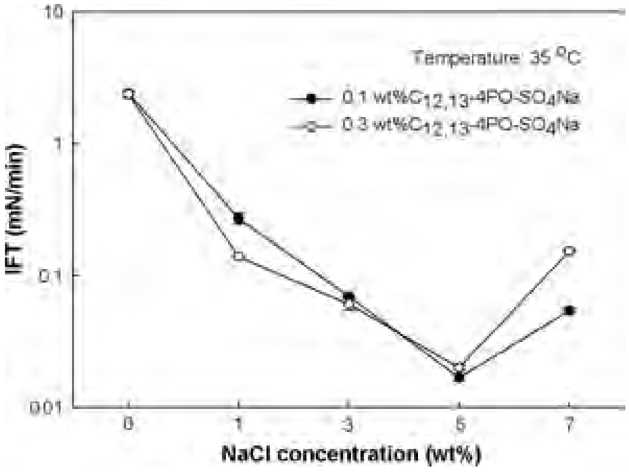

Fig. 3 The correlation of equilibrium IFT using 0.1 and 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ as a function of salinity at 35 °C

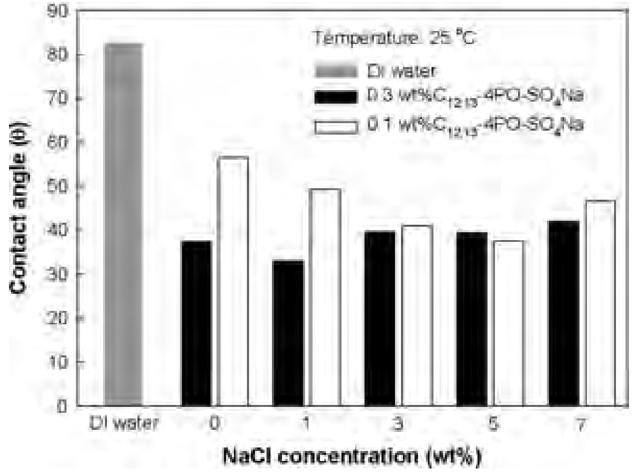

Fig. 4 Contact angle of 0.1 and 0.3 wt% surfactant solution on methyl palmitate surface at 25 °C as a function of salinity

respectively. So, wettability may be a factor in detergency and the simple contact angle measurement may be predictive of cleaning efficiency which would be helpful in formulation development.

Effects of Fabric Type and Washing Temperature on Detergency Performance

Figure 5 shows the effect of washing temperature on oil removal and oil redeposition for polyester and cotton fabrics in surfactant solutions of 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ with 1 and 5 wt% NaCl concentrations and of 0.1 wt% $C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl concentration. The washing temperature range of 15–50 °C was studied in order to cover both solid and liquid states of methyl palmitate (melting point of 30 °C). The oil removal increased with increasing wash temperature for both studied fabrics using the washing solution containing 0.3 and 0.1 wt% surfactant with 5 wt% NaCl concentrations. The detergency performance on the cotton was slightly higher than that on the polyester fabric for any wash temperature. For the washing solution having 0.3 wt% surfactant and 1 wt% NaCl, the detergency performance on the cotton fabric reached a maximum level around the soil melting point (30 °C), but did not change substantially with temperature above the melting point. For polyester fabric with the washing solution of 0.3 wt% surfactant and 1 wt% NaCl, the oil removal increased with increasing washing temperature from 15 to 25 °C. However, detergency decreased dramatically as temperature increased further from 25 to 30 °C. After reaching this minimum oil removal at the melting point, detergency slightly increased as temperature increased further beyond the melting point. This somewhat surprising minimum in detergency is confirmed by photographs of washed polyester at different washing temperatures as shown in Fig. 6.

For all surfactant systems on cotton and two of the three systems on polyester, oil removal generally increases with increasing temperature which is generally true in detergency of different soils. However, this temperature inversion effect has been previously observed on hydrophobic fabric. Morris and Prato [3] found that the best removal of particulate and oily soil from cotton fabric was at high temperatures, whereas the nonpolar fraction of oily soil removed from polyester was better at low wash temperature. Illman *et al.* [36] and Gordon *et al.* [37] found that nonpolar sebum was more easily removed from Dacron or Nylon in cold water than hot water. This was attributed to the diffusion of liquid oil into the interior of polyester at high temperatures, causing the oil to have poor contact with the surfactant solution [38].

In our study, the soil was dissolved in a volatile solvent, the fabric immersed in the solvent/soil mixture, then the solvent evaporated at 25 °C, below the oil melting point. So, when the soil was deposited on the fabric upon evaporation of the solvent, it was a solid. It was suspected that this solid did not incorporate itself into the fabric fibers as a liquid soil would. So, in separate experiments, after the soiling procedure, each fabric was heated up to 40 °C so the soil became liquefied and could diffuse/imbibe into the fabric weave, then cooled to the temperature of the detergency experiment. As shown in Table 2, below the melting point, the oil removal was lower than with normal soiling procedures but at a high wash temperature, detergency was increased around 10%. We conclude that if the soil is a liquid without solvent and allowed to contact the hydrophobic fabric before the system is cooled, as would be the case with sebum and warm hamburger/bacon grease, below the melting point, it is much more difficult to remove the soil than if the soil only contacts the fabric as a solid below the melting point. That this effect is only observed on hydrophobic polyester fabric and not on cotton indicates that the hydrophobic monoglyceride soil has a much stronger attractive interaction with the hydrophobic fabric than a hydrophilic fabric. A broader range of soil polarities would need to be studied to determine the generality of this effect and if monoglycerides/triglycerides are peculiar in their interaction with polyester compared to say hydrocarbon soils. And the temperature inversion effect is not observed for every surfactant system (one out of three here). So, it is recommended that a systematic soiling procedure be used for studies of waxy solids when temperature ranges below the melting point are included.

In a comparison of the two NaCl concentrations in the 0.3 wt% surfactant solution (Fig. 5), for any studied fabric, the detergency performance at 5 wt% NaCl was higher than that at 1 wt% NaCl at a washing temperature above the melting point due to the low IFT values of 0.009–0.09 mN/m at 5 wt% NaCl as compared to those of around 0.1 mN/m at 1 wt% NaCl (Fig. 3). In contrast, for any washing temperature below the melting point of 30 °C, the oil removal at 5 wt% NaCl was lower than that at 1 wt% NaCl, especially on the polyester fabric. The oil removal on the cotton fabric was higher than that on the polyester fabric under studied conditions except at washing temperatures below the melting point with the NaCl concentration of 1 wt%. There is apparently a high affinity of the liquid methyl palmitate and hydrophobic polyester as compared to that on the hydrophilic cotton fabric. However, at a temperature lower than the melting point, the oil removal for the polyester fabric was much higher than that on the cotton fabric, suggesting that the contact of the solid methyl palmitate with the fabric is less than for liquid methyl palmitate. This supports the same conclusion reached from different soiling procedures about solid soil not interacting well with polyester.

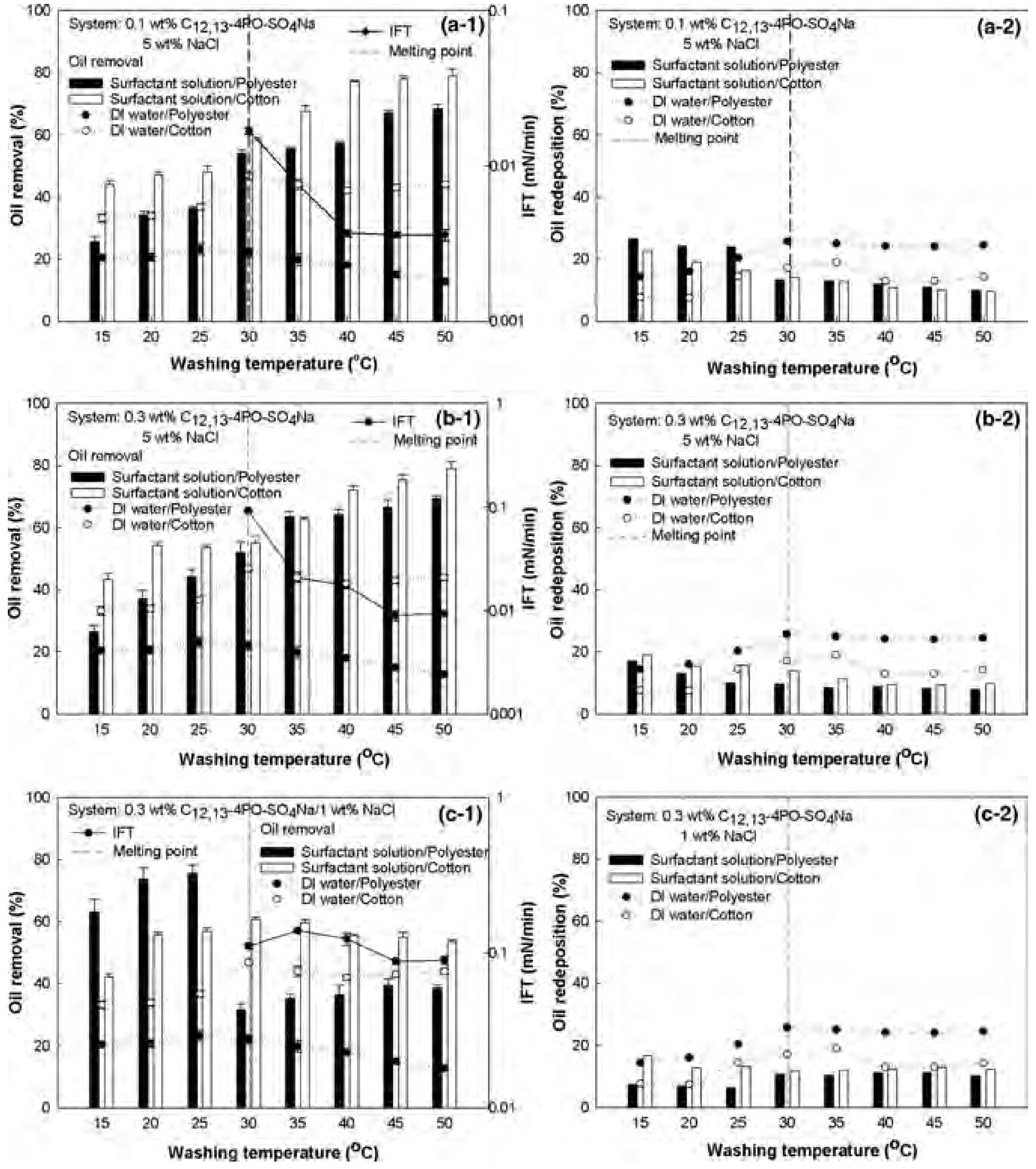

Fig. 5 Oil removal and redeposition as a function of washing temperature in relation to equilibrium IFT at **a** 0.1 wt% $C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl, **b** 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl, and **c** 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ with 1 wt% NaCl on both test fabrics of cotton and polyester

The use of surfactant showed a much higher oil removal at any washing temperature as compared to DI water. For DI water systems, the oil removal slightly increased and reached a maximum level at about the melting point for both test fabrics. Beyond the melting point (30 °C), the oil removal on polyester fabric slightly decreased with further increasing washing temperature. Therefore, the best conditions found at any temperature below the melting point

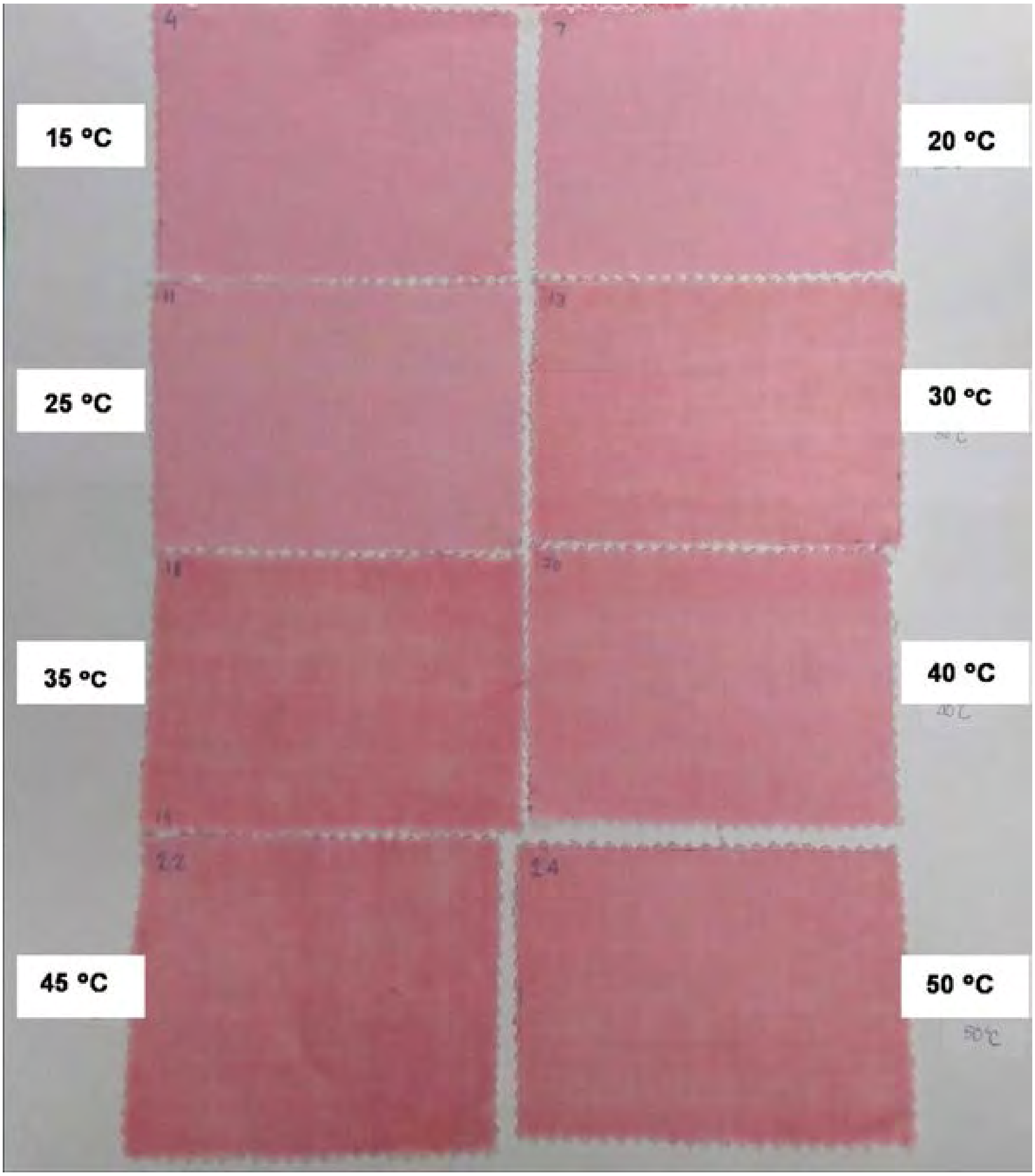

Fig. 6 Picture of washed fabrics at different washing temperatures of 0.3 wt% $C_{12,13}$-4PO-SO_3Na with 1 wt% NaCl

Table 2 The effect of soiling procedure on detergency performance for polyester

Washing temperature (°C)	Oil removal (%)	
	Not heated soiling (25°)	Heated soiling (40°)
15	63.3 ± 4.12	30.96 ± 2.84
20	73.79 ± 3.69	35.23 ± 1.91
25	75.50 ± 2.80	30.05 ± 3.88
30	31.63 ± 1.84	40.90 ± 3.91
35	35.32 ± 1.24	50.95 ± 1.73
40	36.40 ± 3.02	46.74 ± 2.08

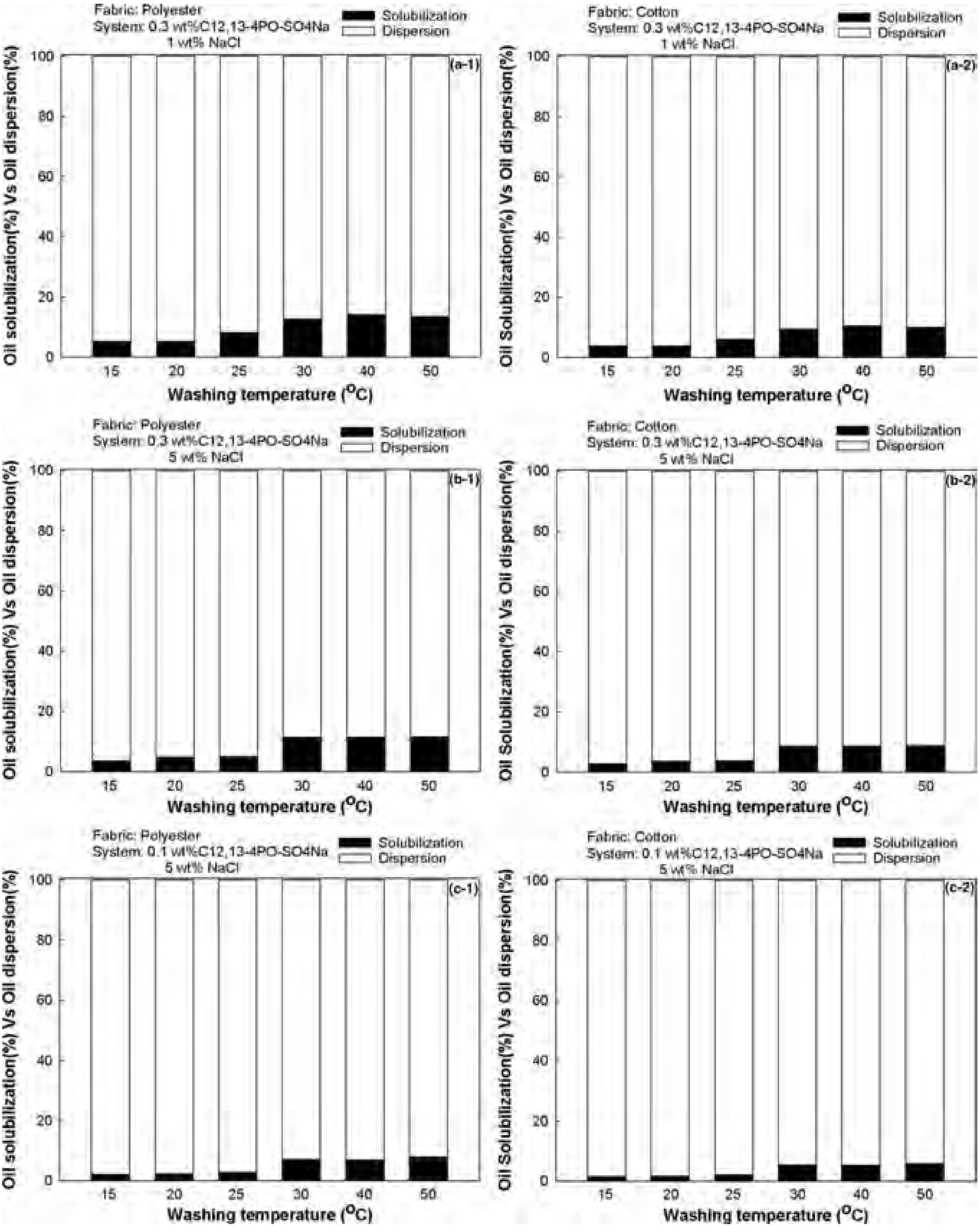

Fig. 7 Solubilized portions and unsolubilized portions of removed oil at 20 min; **a** 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ with 1 wt% NaCl, **b** 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl, and **c** 0.1 wt% $C_{12,13}(PO)_4SO_4Na$ with 5 wt% NaCl on both test fabrics of cotton and polyester

Table 3 The ratio of oil solubilization at 20 min to equilibrium oil solubilization with different surfactant systems

Temperature (°C)	Oil solubilization (g/L)		Ratio
	At 20 min	At equilibrium	(At 20 min/at equilibrium)
0.3 wt% $C_{12,13}$-4PO-SO_4Na/1 wt% NaCl			
20	0.0235 ± 0.0035	0.190 ± 0.020	0.1236
25	0.0365 ± 0.0034	0.342 ± 0.012	0.1069
30	0.0570 ± 0.0014	0.226 ± 0.016	0.2519
40	0.0635 ± 0.0233	0.662 ± 0.030	0.0959
50	0.0605 ± 0.0149	0.634 ± 0.033	0.0955
0.3 wt% $C_{12,13}$-4PO-SO_4Na/5 wt% NaCl			
20	0.0210 ± 0.0014	0.304 ± 0.023	0.0691
25	0.0220 ± 0.0056	0.262 ± 0.005	0.0841
30	0.0510 ± 0.0010	0.272 ± 0.004	0.1872
40	0.0520 ± 0.0014	0.506 ± 0.006	0.1028
50	0.0500 ± 0.0028	0.532 ± 0.038	0.0940
0.1 wt% $C_{12,13}$-4PO-SO_4Na/5 wt% NaCl			
20	0.0105 ± 0.0021	0.109 ± 0.008	0.0959
25	0.0125 ± 0.0035	0.104 ± 0.026	0.1202
30	0.0318 ± 0.0017	0.123 ± 0.008	0.2585
40	0.0312 ± 0.0024	0.160 ± 0.009	0.1950
50	0.0350 ± 0.0036	0.233 ± 0.012	0.1502

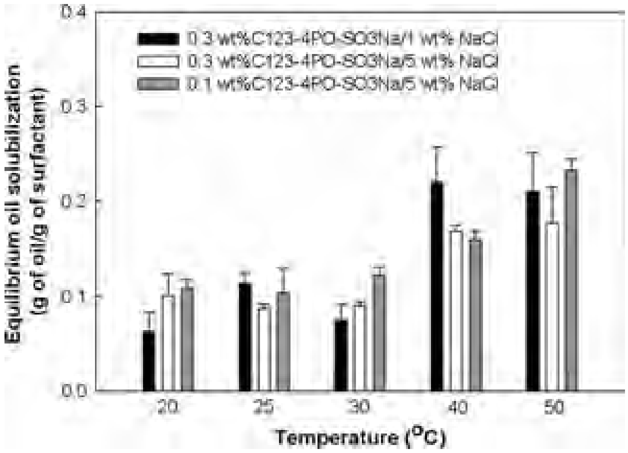

Fig. 8 Equilibrium oil solubilization in different surfactant systems as a function of temperature

were a 0.3 wt% surfactant concentration with a 1 wt% NaCl concentration whereas the same surfactant concentration of 0.3 and 5 wt% NaCl were found to be better for a washing temperature above the melting point. Generally, it is known that an increase in temperature results in increasing hydrophilicity of anionic surfactants but nonionic surfactants have the opposite trend. The studied extended surfactant has the polypropylene oxide groups inserted between the hydrophobic tail and hydrophilic head group, making it less sensitive to temperature than conventional anionic surfactants [39]. This may suggest that the studied extended surfactant has mixed properties between anionic and nonionic surfactants, explaining good oily detergency over a wide range of washing temperatures.

Figure 5c-2 shows the oil redeposition as a function of washing temperature for both DI water solution and 0.3 wt% surfactant with 1 wt% NaCl concentrations for both polyester and cotton fabrics. For DI water, the oil redeposition reached the maximum at about the melting point for both studied fabrics. For the surfactant solution, the oil redeposition on the cotton fabric reached a slight minimum at the melting point whereas the oil redeposition on the polyester fabric showed a sharp decrease with increasing temperature at the melting point, similar to the decrease in oil removal at the melting point. For cotton, this anomalous behavior is not seen. As shown in Fig. 5a-2, b-2, 0.3 wt% surfactant with 1 wt% NaCl concentration and 0.1 wt% surfactant and 5 wt% NaCl concentration, the oil redeposition generally decreased with increasing temperature just as oil removal generally increased with temperature. So the surprising temperature inversion observed at the melting point, observed only for polyester, is evidenced in both oil removal and oil redeposition.

Solubilization Results

Figure 7 shows both solubilized and unsolubilized portions of removed oil in different washing solutions at different washing temperatures for both test fabrics at 20 min. For any washing temperature, most of removed oil was found to be in a separate dispersed phase (either emulsified liquid droplets or dispersed solid particles) with a very small portion solubilizing in micelles. The solubilized portion slightly increased with increasing washing temperature. An increase in surfactant concentration from 0.1 to 0.3 wt% increased the solubilization portion of removed oil. This is because an increase in surfactant concentration simply increases the concentration of micelles, leading to an increase in oil solubilization. The results of most removed oil being in free oil particles suggest that the dispersion stability of detached oil particles plays an important role in the overall detergency performance. The differences between the oil solubilization at 20 min and the equilibrium oil solubilization at different temperatures are shown in Table 3. For all studied systems, equilibrium oil solubilization was attained at a very long time (about 24 h). Most of the oil solubilization values at 20 min were around 10% of the equilibrium oil solubilization values, suggesting that the washing time used in the washing experiment as well as in actual application is too short for effective solubilization so most detached oil is in unsolubilized form. Comparing the three surfactant systems in term of g of oil/g of surfactant in Fig. 8 shows that at any temperature below the melting point (∼30 °C) for all studied surfactant systems, the equilibrium oil solubilization values were almost unchanged with temperature and significantly lower than those at any temperature higher than the melting point. With increasing washing temperature above the melting point, the equilibrium oil solubilization value considerably increased and tended to level off at a temperature around 40–50 °C.

Particle Size Distribution of Detached Oil Particles after Wash Step

Table 4 shows the particle size distribution of methyl palmitate particles suspended in the washing solution after the 20 min wash step for both fabrics using either surfactant or DI water at 25 °C. At 25 °C, the solid nature of the particles of methyl palmitate made it possible to measure the particle size distribution. For any wash system, the particle size distribution of the methyl palmitate solid particles detached from any fabric consisted of a trimodal distribution or three ranges of particle sizes (1–5, 5–100, 100–600 μm). Compared to the surfactant formulation, when DI water was used in the wash step, the detached particles of methyl palmitate had larger sizes in the ranges of 5–100 and 100–600 μm with mean sizes of about 100 and 120 μm for the cotton and polyester fabrics, respectively. Interestingly, the use of surfactant resulted in particle sizes of the detached methyl palmitate solid particles being about one third to one fourth of those of the DI water system. The results suggest that surfactant solution penetrates the methyl palmitate by wetting, the soil is then

Table 4 Particle size distribution and averaged sizes of methyl palmitate after washing step with DI water and surfactant solution with various salinities at 25 °C

Washing solution	Cotton							Polyester						
	1–5 μm		5–100 μm		100–600 μm		Mean size (μm)	1–5 μm		5–100 μm		100–600 μm		Mean size (μm)
	Size (μm)	Vol. (%)	Size (μm)	Vol. (%)	Size (μm)	Vol. (%)		Size (μm)	Vol. (%)	Size (μm)	Vol. (%)	Size (μm)	Vol. (%)	
De-ionized water	2.32 ± 0.02	9.45	23.2 ± 1.11	58.4	282 ± 5.28	32.2	101 ± 3.88	2.76 ± 0.48	6.50	30.0 ± 0.11	57.1	280 ± 26.8	36.4	120 ± 17.8
$C_{12,13}(PO)_4SO_4Na$	2.46 ± 0.01	31	10.6 ± 0.13	60.8	309 ± 1.84	8.19	36.2 ± 1.78	2.51 ± 0.01	24.1	11.8 ± 0.06	64.1	313 ± 12.2	11.7	45.8 ± 1.41
$C_{12,13}(PO)_4SO_4Na$/ 1wt %NaCl	2.39 ± 0.05	21.5	15.6 ± 0.51	70.5	276 ± 9.31	8.02	29.4 ± 2.47	2.37 ± 0.01	28.1	13.3 ± 0.35	62.1	313 ± 8.07	9.79	40.0 ± 0.55
$C_{12,13}(PO)_4SO_4Na$/ 3wt %NaCl	2.43 ± 0.11	21.3	14.3 ± 0.77	74.2	223 ± 3.48	4.48	21.0 ± 0.67	2.39 ± 0.01	26.4	13.1 ± 0.17	63.6	344 ± 4.67	10.0	44.4 ± 1.73
$C_{12,13}(PO)_4SO_4Na$/ 5wt %NaCl	2.40 ± 0.04	32.7	12.6 ± 1.98	61.8	289 ± 10.2	5.53	24.1 ± 3.46	2.37 ± 0.01	23.9	14.3 ± 0.51	66.7	335 ± 3.25	8.81	38.7 ± 1.81
$C_{12,13}(PO)_4SO_4Na$/ 7wt %NaCl	2.37 ± 0.01	34.8	13.6 ± 0.04	59.9	348 ± 2.66	5.34	24.7 ± 2.62	2.38 ± 0.11	20.2	15.8 ± 3.51	71.3	289 ± 25.9	8.50	37.2 ± 6.68

Table 5 Point of zero charge (PZC) and zeta potential of methyl palmitate, cotton, and polyester in various solutions at 25 °C

Properties	Cotton	Polyester	Methyl palmitate
Point of zero charge (PZC)	2.90[a]	2.40[a]	2.20
Zeta potential (mV) in:			
DI water	−20.3 ± 5.0	−50.0 ± 5.0	−46.2 ± 2.7
0.1 wt% $C_{12,13}$-4PO-SO_4Na	−73.5 ± 6.7	−139 ± 7.6	−157 ± 5.5
0.1 wt% $C_{12,13}$-4PO-SO_4Na/1 wt% NaCl	−54.9 ± 3.4	−60.9 ± 7.2	−57.0 ± 4.3
0.1 wt% $C_{12,13}$-4PO-SO_4Na/3 wt% NaCl	−48.0 ± 4.8	−54.4 ± 4.6	−53.7 ± 2.0
0.1 wt% $C_{12,13}$-4PO-SO_4Na/5 wt% NaCl	−33.3 ± 1.0	−33.1 ± 2.8	−34.1 ± 2.3
0.1 wt% $C_{12,13}$-4PO-SO_4Na/7 wt% NaCl	−30.8 ± 2.7	−28.7 ± 2.5	−29.9 ± 1.2

[a] Data from previous work [14]

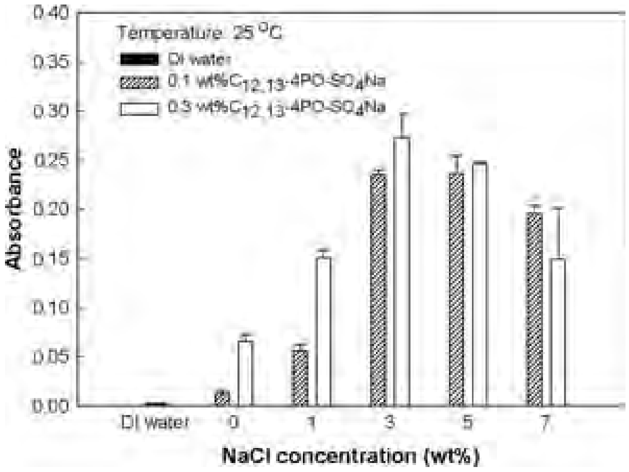

Fig. 9 Dispersion stability (absorbance) of methyl palmitate particles in surfactant solutions as a function of salinity as compared to DI water at 25 °C

dislodged as small particles or droplets, so the small particle size correlates with good wettability leading to high detergency efficiency.

Point of Zero Charge and Zeta Potential Results

Table 5 shows the point of zero charge (PZC) and zeta potential values of methyl palmitate, cotton, and polyester particles in various solution systems at 25 °C (pH 4–6). The PZC values of methyl palmitate, cotton, and polyester were 2.20, 2.90, and 2.40, respectively, indicating that the net surface charges of these three materials are always negative in detergency experiments because of the much higher pH values of both DI water and the studied extended surfactant solutions. The magnitude of the zeta potential of methyl palmitate is high despite it being fairly hydrophobic (contact angle with water of 82°) because of the ester functional group in methyl palmitate which is hydrolyzed into carboxyl and hydroxyl groups to provide negative charges [14, 15, 40, 41]. When DI water was replaced by the 0.1 wt% surfactant solution, the zeta potential of methyl palmitate became more negative from −46.2 to −157 mV because of the anionic surfactant adsorption. The zeta potential values of both cotton, and polyester in the studied extended surfactant solution became more negative as compared to those in DI water and they also increased when the surfactant concentration increased [42]. This is probably due to higher surfactant adsorption on the solid with higher surfactant concentration, although higher adsorption doesn't necessarily occur since concentrations are well above the CMC. In contrast, with increasing NaCl concentration for any fixed extended surfactant concentration, the zeta potential of methyl palmitate, cotton, and polyester became less negative, due to compression of the double layer or reduction of Debye length next to the surface with increasing ionic strength [43, 44]. A high absolute zeta potential indicates that electrostatic repulsion could be an important factor in dispersion stability [45, 46].

Dispersion Stability

Figure 9 shows the dispersion stability (absorbance) of methyl palmitate solid particles (in terms of average absorbance values) as a function of salinity in the two surfactant systems (0.1 and 0.3 wt%) at 25 °C. The higher the absorbance, the greater the concentration of particles dispersed in the aqueous phase and thus the higher the dispersion stability. The presence of extended surfactant without added NaCl only marginally improved the dispersion stability of methyl palmitate solid particles as compared to DI water despite the fact that the zeta potential is much more negative in the presence of surfactant. Increasing NaCl concentration can greatly improve the dispersion stability; the maximum dispersion stability was found in the salinity range of 3–5 wt% which also produced the best detergency performance. So, dispersion stability is an important component of detergency since the dominant mechanism of solid removal is as particles, not through solubilization. However, the zeta potential decreases in magnitude with increasing NaCl concentration. Comparing effects of surfactant and NaCl concentrations on zeta potentials and dispersion stability lead to the important conclusion that electrostatic stabilization of the dispersed particles is not the dominant factor in dispersion stability. Dispersion stability is not highest when the zeta potential is at maximum value. Parfitt and Wharton [47] studied the dispersion of solid particles in a surfactant solution and found that the dispersion followed a three-stage process. First, the wettability of solid particle surface occurred, as reflected by the corresponding contact angle. The surfactant solution is better able to penetrate into inter-particle clusters and crevices due to the reduction of the contact angle. Second, the solid particles are suspended in the solution by wetting, and thus dispersion stability occurs. Therefore, deaggregation of the solid particle is required to achieve a good dispersion by repulsive force between charged particles. After the solid particles have been dispersed in the solution, the danger is that they will coagulate (aggregate) and redeposit. Therefore, the wettability (contact angle), particle size distribution, and dispersion stability of the particles are important to detergency efficiency.

Visual Observations

Figure 10 shows pictures of the washing solutions after the wash step using DI water (Fig. 10a) and two surfactant solutions (0.1 wt% surfactant with 5 wt% NaCl and 0.3 wt% surfactant with 1 wt% NaCl) at temperatures

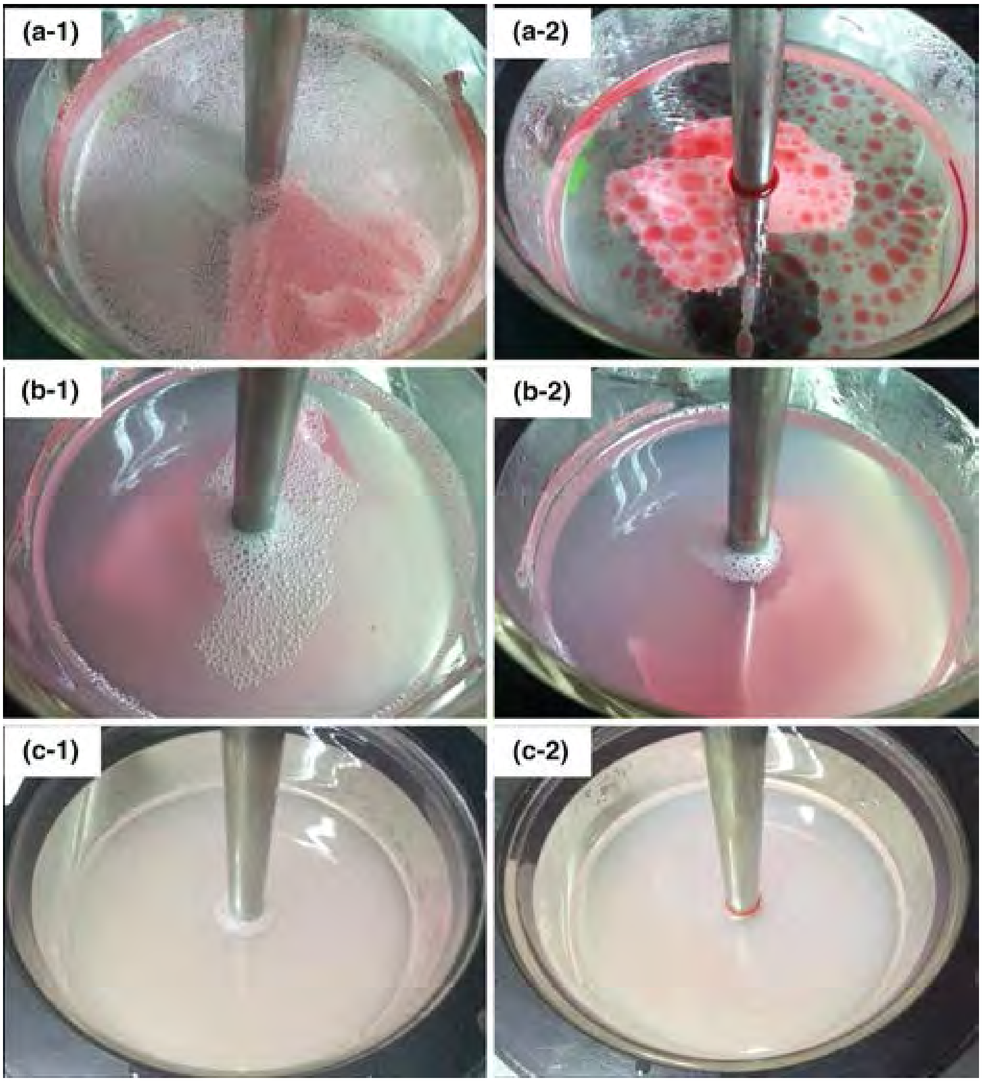

Fig. 10 Photographs of washing solutions after the wash step: **a-1** at below the melting point (25 °C) in DI water, **a-2** above the melting point (35 °C) in DI water, **b-1** below the melting point (25 °C) in 0.1 wt% $C_{12,13}(PO)_4SO_4Na$ and 5 wt% NaCl, **b-2** above the melting point (35 °C) in 0.1 wt% $C_{12,13}(PO)_4SO_4Na$ and 5 wt% NaCl, **c-1** below the melting point (25 °C) in 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ and 1 wt% NaCl, **c-2** above the melting point (35 °C) in 0.3 wt% $C_{12,13}(PO)_4SO_4Na$ and 1 wt% NaCl

below and above the oil's melting point. In DI water, the removed oil was found mostly in solid particles floating on the surface of the washing solution with relatively large particle sizes at 25 °C and much larger liquid droplets at 35 °C. For detergency with surfactant solutions, the removed oil was found to suspend in the washing solution with much smaller particles and without either solid or liquid methyl palmitate particles or droplets floating on the surface.

Mechanistic Insights

Results on this paper shows the relationships between the removal mechanism of solid fat soil below and above the soil melting point. Above the melting point, lower IFT results in better detergency with varying temperature or salinity. Therefore, roll-up of liquid soil is an important mechanism [6–13]. Below the melting point, the detachment of soil as solid particles occurs by surfactant penetration, leading to the soil breaking up and floating away from the fabric surface into solution as small particles [48–50]. Surfactant and salinity improves wetting, dispersion stability, and decreases detached particle size. Unlike particulate soil, electrostatics are not the primary driving force for detergency.

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