DETERGENCY OF MIXED OILY AND PARTICULATE SOILS BY SINGLE AND MIXED SURFACTANT SYSTEMS

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A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole
2018

Thesis Title:	Detergency of Mixed Oily and Particulate Soils by Single and Mixed Surfactant Systems
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Program:	Petrochemical Technology
Thesis Advisors:	Assoc. Prof. Boonyarach Kitiyanan Prof. Sumaeth Chavadej

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Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

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ABSTRACT

5971014063: Petrochemical Technology Program
Thanawan Teerasathittham: Detergency of Mixed Oily and Particulate Soils by Single and Mixed Surfactant Systems
Thesis Advisors: Assoc. Prof. Boonyarach Kitiyanan, Prof. Sumaeth Chavadej, and Prof. John F. Scamehorn 67 pp.
Keywords: Detergency/ Mixed Soils/ Mixed Surfactant

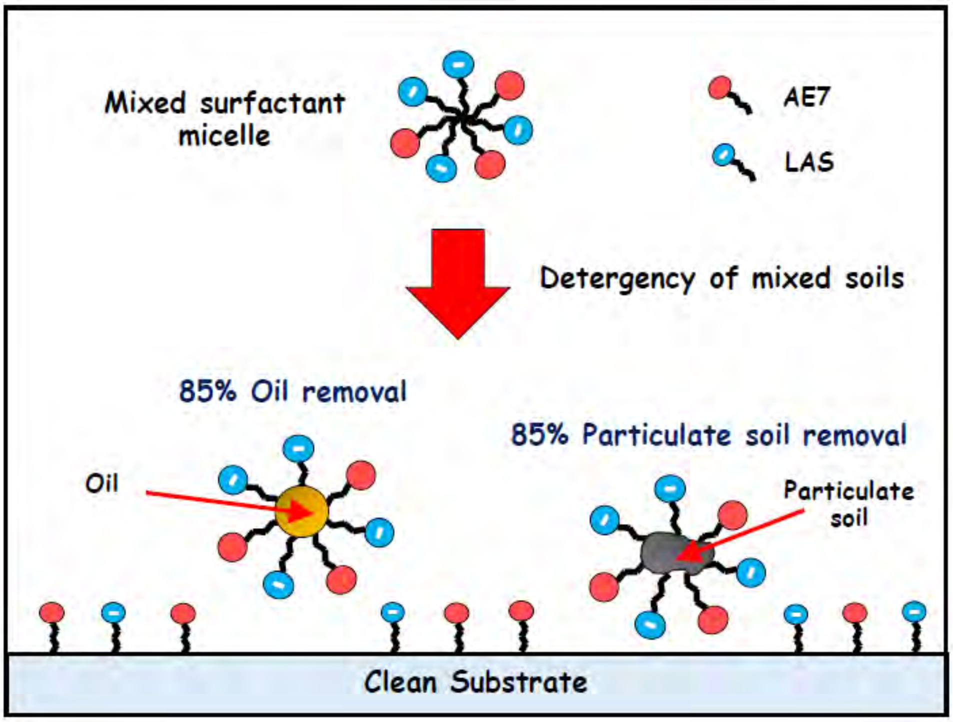
This research studies the detergency performance of mixed surfactants of (anionic and nonionic surfactants) for mixed oily and particulate soils on polyester/cotton blend fabric, and compares with a commercial liquid detergent. Palm oil and kaolinite are used as representatives of oily soil and particulate soil, respectively. The anionic surfactants used in this study are methyl ester sulfonate (MES), linear alkyl benzene sulfonate (LAS) and sodium dodecyl sulfate (SDS). The nonionic surfactants are alcohol ethoxylate 7EO (AE7) and alcohol ethoxylate 9EO (AE9). The effect of surfactant concentrations, NaCl concentration, and mixing ratios of the selected surfactant formulations on detergency performance are investigated. The mixed surfactant system of LAS and AE7 with a 0.3 wt. % total surfactant concentration provides the maximum detergency performance at low salinity of 2 wt. % NaCl. Interestingly, the particulate soil removal for any mixing ratios of all selected surfactant systems could exceed 85%, which is higher than those from either any single surfactant or the commercial liquid detergent. This is possibly because of the synergistic effect between the ethoxylated head group of AE7 and sulfonate head groups of LAS that balance the electrostatic repulsion, leading to lowering the free energy of the system. In addition, the percentages of detergency and total oil removal are relatively constant with the ratio of mixed surfactants.

บทคัดย่อ

ธนวรรณ ธีรสถิตย์ธรรม : การซักฟอกของสิ่งปนเปื้อนผสม โดยใช้สารลดแรงตึงผิวแบบไม่ผสมและแบบผสม (Detergency of Mixed Oily and Particulate Soils by Single and Mixed Surfactant Systems) อ. ที่ปรึกษา : รศ.ดร. บุนยรัชต์ กิติยานันท์, ศ.ดร. สุเมธ ชวเดช และ ศ.ดร. John F. Scamehorn 67 หน้า

งานวิจัยนี้ศึกษาประสิทธิภาพของการชำระล้างสิ่งปนเปื้อนผสมของน้ำมันและดินขาวบนผ้าโพลีเอสเตอร์ผสมผ้าฝ้าย โดยใช้สารลดแรงตึงผิวแบบไม่ผสมและแบบผสม โดยนำมาเปรียบเทียบประสิทธิภาพกับผลิตภัณฑ์ผงซักฟอกในท้องตลาด ซึ่งน้ำมันปาล์มและดินขาวถูกนำมาใช้เป็นตัวจำลองคราบสกปรกแบบน้ำมันและอนุภาคของแข็งตามลำดับ สารลดแรงตึงผิวประจุลบที่ศึกษาได้แก่ เมทิลเอสเทอร์ซัลโฟเนตหรือเอ็มอีเอส ลิเนียร์แอลคิลเบนซีนซัลโฟเนตหรือแอลเอเอส และโซเดียมโดเดซิลซัลเฟตหรือเอสดีเอส และสารลดแรงตึงผิวไม่มีประจุได้แก่ แอลกอฮอล์อีท็อกซีเลต 7EOหรือเออีเจ็ด และ แอลกอฮอล์อีท็อกซีเลต 9EOหรือเออีเก้า โดยทำการศึกษาประสิทธิภาพของการชำระล้างนี้ที่ความเข้มข้นของสารลดแรงตึงผิว ความเข้มข้นของโซเดียมคลอไรด์ และอัตราส่วนการผสม ระหว่างสารลดแรงตึงผิวประจุลบและไม่มีประจุที่แตกต่างกัน ซึ่งสารลดแรงตึงผิวชนิดผสมของลิเนียร์แอลคิลเบนซีนซัลโฟเนตหรือแอลเอเอสและแอลกอฮอล์อีท็อกซีเลต 7EOหรือเออีเจ็ด ที่ความเข้มข้น 0.3 เปอร์เซ็นต์โดยน้ำหนักให้ประสิทธิภาพในการชำระล้างสูงสุดที่ปริมาณความเข้มข้นของโซเดียมคลอไรด์ 2 เปอร์เซ็นต์โดยน้ำหนัก ในกรณีของประสิทธิภาพของการชำระล้างอนุภาคของแข็งที่ทุกอัตราส่วนของสารลดแรงตึงผิวผสมให้ประสิทธิภาพสูงมากกว่า 85 เปอร์เซ็นต์ ซึ่งให้ค่าสูงกว่าสารลดแรงตึงผิวชนิดแบบไม่ผสมและผลิตภัณฑ์ผงซักฟอกในท้องตลาด แต่อย่างไรก็ตามอัตราส่วนของสารลดแรงตึงผิวผสมที่แตกต่างกันไม่ได้ส่งเสริมค่าประสิทธิภาพของการชำระล้างและประสิทธิภาพของ การชำระล้างน้ำมันออกจากผ้า

GRAPHICAL ABSTRACT



The synergistic effect of mixed nonionic and anionic surfactant system to remove mixed soils from substrate

ACKNOWLEDGEMENTS

Firstly, I would like to express my very great appreciation to all of my advisors, Prof. Sumaeth Chavadej, Assoc. Prof. Boonyarach Kitiyanan and Prof. John F. Scamehorn for their valuable guidance, enthusiastic encouragement and support of this research work. Furthermore, I would like to thank Ms. Jarussri Chanwattanakit for her advice and assistance in keeping my progress on schedule. Without their precious supports, it would not be possible to conduct this research.

Besides my advisor, I would like to thank my lovely friend in SC group at The Petroleum and Petrochemical College, Chulalongkorn University for their encouragement and willingly assistance. In addition, I wish to thank my parents and my sister for their support and encouragement throughout my study and my life.

Finally, I would like to grateful for the full scholarship and full funding of the thesis work provided by the Petroleum and Petrochemical College. This thesis work is funded by the Petroleum and Petrochemical College and Center of Excellence on Petrochemical and Materials Technology and The Thailand Research Fund.

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CHAPTER I
INTRODUCTION

Detergency is defined as cleaning the surface of a solid object, using a solution with specific agents. In cleaning, the detergent removes unwanted substances (soils) from surface (fabrics) and keeps soils in suspension in water to prevent re-deposition on clothes (Louis Ho Tan Tai, 2000). Soils can be categorized into four types: particulate soils, non-particulate soils, oils, and stains. Different types of soils requires different formulations to remove. Moreover, detergency cannot be described by a single mechanism but rather a number of various mechanisms in which surfactants play an important role (Rosen, 2004). For oily soil removal, there are major three mechanisms, which are roll-up, emulsification, and solubilization. For particulate soil removal, the main mechanism is electrostatic repulsion.

The detergency effectiveness is dependent on several factors, such as type of soil, fabrics, temperature, type and concentration of the surfactant system, water hardness, hydrodynamic conditions, electrolyte level, as well as composition of the surfactant solution (Tongcumpou, 2003 and Thompson, 1994). The maximum detergency corresponds to the optimum conditions where the minimum oil/water IFT of the microemulsion exists. For an anionic surfactant system, the minimum IFT can achieve at the optimum salinity and anionic surfactants are good for particulate soils removal. In a system with nonionic surfactants, the optimum detergency occurs at the phase inversion temperature (PIT) and nonionic surfactants are excellent for oily soils removal (Tanthakit, 2008).

The purpose of this research is to remove mixed soils from fabrics by using single and mixed surfactants of anionic surfactants such as methyl ester sulfonate (MES), sodium dodecyl sulfate (SDS), and, sodium dodecylbenzenesulfonate (LAS) with nonionic surfactant of alcohol ethoxylate (AE). In this study, kaolinite clay and palm oil are selected to represent hydrophilic particulate soil and hydrophobic oil, respectively. A polyester/cotton blend [65/35] is used as representative of a testing fabric in detergency experiment. Cotton and polyester are used as a model hydrophilic fabric and hydrophobic fabric, respectively. The critical micelle concentration (CMC), dynamic interfacial tension (IFT) and zeta potential are correlated to detergency performance as a function of different surfactant concentrations and salinity concentrations. In addition, the commercial liquid detergent product is also compared with the selected surfactant formulations.

CHAPTER II
LITERATURE REVIEW

2.1 Surfactants

The surfactant or surface-active agent is one of the most important components of a detergent. Their effect depends on their structure, the chain length, the degree of branching of the hydrophobic part, and the hydrophilic group nature. It has an amphiphilic character, which means that it is composed of a polar (hydrophilic group) and an apolar (hydrophobic group) part as shown in Figure 2.1. Surfactants can be classified into anionics, cationics, nonionics, and zwitterionics, depending on the polar head group (Ishiguro *et al*., 2016).

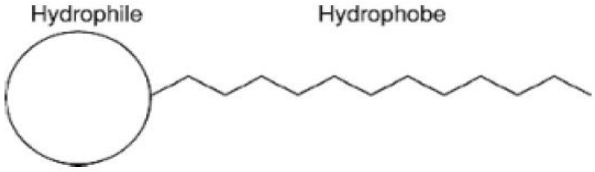


Figure 2.1 Structure of surfactant.

2.1.1 Anionic Surfactants

Anionic surfactants have a negatively charge on their hydrophilic group. They are great for particulate soils removal, for example, linear alkyl benzene sulfonate, methyl ester sulfonate, fatty acid soap, etc.

2.1.2 Cationic Surfactants

Cationic surfactants have a positively charge on their hydrophilic group. They are great for oily soil removal, for example, quaternary monoalkyl ammonium chloride, cetyl trimethylammonium bromide, etc.

2.1.3 Nonionic Surfactants

Nonionic surfactants have no charge on their hydropholic group. They are excellent for grease removal, for example, fatty alcohol ethoxylate, amine oxide, alkyl monoethanolamide, etc.

2.1.4 Zwitterionic Surfactants or Amphoteric Surfactants

These surfactants have both a negative and a positive charge on their hydrophilic group, or no charge depending on pH of the water or the acidity. They are effectively for high amounts of acids, alkalis, and electrolytes, for example, amidopropyl betaine, alkyl sulfobetaine, etc.

2.2 Classification of Soils

Soils are the unwanted materials that is to be removed from the substrate and can be classified into four groups: oily soils, particulate soils, non-particulate soils and stains.

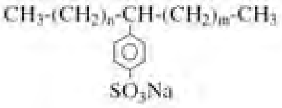
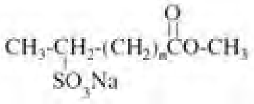
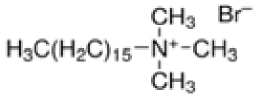
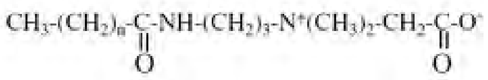
2.2.1 Oily Soils

Oily soils are usually organic and very hydrophobic liquid. So they cannot dissolve or well mix with water, for example, hydrocarbons, saturated or unsaturated fatty acids, ester of fatty acids and alcohols.

2.2.2 Particulate Soils

Particulate soils are usually inorganic solid. They have several properties such as size, shape, as well as surface geometry of soil, for example, silica, alumina, clay, carbon black, dust. They are not soluble either in water or in organic solvent.

Table 2.1 Common Surfactants Used in Detergent Formulations (Showell, 2006)

Anionic	
Linear Alkyl Benzene Sulfonate	
Methyl Ester Sulfonate	 $CH_3\text{-}\underset{SO_3Na}{CH_2}\text{-}(CH_2)_n\overset{O}{\overset{\|}{C}}O\text{-}CH_3$
Fatty Acid Soap	 $CH_3\text{-}(CH_2)_n\overset{O}{\overset{\|}{C}}ONa$
Cationic	
Quaternary monoalkylammonium chloride	$CH_3\text{-}(CH_2)_n\text{-}N^+(CH_3)_3Cl^-$
Cetyl Trimethylammonium Bromide	 $H_3C(H_2C)_{15}-\underset{CH_3}{\overset{CH_3}{N^+}}-CH_3\ Br^-$
Nonionic	
Fatty Alcohol Ethoxylate	$CH_3\text{-}(CH_2)_n\text{-}O\text{-}(CH_2\text{-}CH_2O)_nH$
Amine Oxide	$CH_3\text{-}(CH_2)_n\text{-}N(CH_3)_2\rightarrow O$
Alkyl monoethanolamide	 $CH_3\text{-}(CH_2)_n\text{-}\underset{O}{\underset{\|}{C}}\text{-}NH\text{-}CH_2\text{-}CH_2OH$
Zwitterionic or Amphoteric	
Amidopropyl betaine	 $CH_3\text{-}(CH_2)_n\text{-}\underset{O}{\underset{\|}{C}}\text{-}NH\text{-}(CH_2)_3\text{-}N^+(CH_3)_2\text{-}CH_2\text{-}\underset{O}{\underset{\|}{C}}\text{-}O^-$
Alkyl sulfobetaine	 $CH_3\text{-}(CH_2)_n\text{-}N^+(CH_3)_2\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}SO_3^-$

2.2.2.1 Kaolinite

Kaolinite is a hydrous aluminium silicate which has a good physical properties and stable chemical structure. It is the base materials for ceramic, medicine, coated paper, food additive, and toothpaste. Kaolinite is white, soft, and mainly composed of kaolin. The morphology of the kaolin crystal is plate-like particle. Its chemical structure is $Al_2Si_2O_5(OH)_4$ (39.8% alumina, 46.3% silica. 13.9% water) which represents two-layer crystal (silicon-oxygen tetrahedral layer joined to alumina octahedral layer). Figure 2.2 shows the kaolinite structure which held together by hydrogen bonds and Van der Waals interactions.

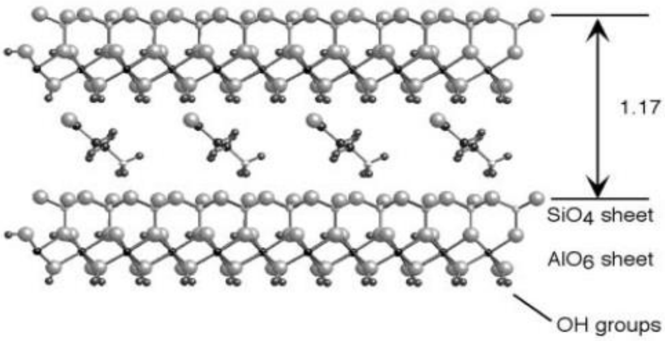


Figure 2.2 Structure of kaolinite (Itagaki, 2001).

2.2.3 Non-particulate Soils

Non-particulate soils are waxy solid contaminants which have properties of liquid and solid, depending on temperature, for example, butter, solidified hamburger or bacon grease, sebum from human skin.

2.2.4 Stains

Stains are unwanted dyestuffs that can form chemical or physical bond between soil and fabric. They are difficult to remove and can destroy the fabric. There are several types of this soil such as wine, blood, coffee, ink, and fruit juices.

2.3 Vegetable Oils

Vegetable oils have been widely used as a cooking oil in household and industrial products. The major component in vegetable oils is triglycerides which consist of three long hydrocarbon chains and a bulky glycerol group. Vegetable oils are semi-solid fats or waxy soils at below their melting points. These points can cause the weak interaction with surfactants in solution due to the liquid oils in waxy soils are entrapped in the solid fat structures. In addition, the removal of vegetable oils is more difficult to remove at above their melting points. This is because of the bulkiness (molecular volume) of hydrophobic and polar nature of vegetable oils (Phan, 2010 and Do, 2015).

Palm oil is widely used in foods such as cooking oils, margarines, shortenings. Its components contain 43% palmitic acid, 41% oleic acid, 4.5% stearic acid, and 9.5% linoleic acid. In general, palm oil is composed of approximately 50% saturated fatty acids, 40% monounsaturated fatty acids, and 10% polyunsaturated fatty acids (Tanthakit, 2010 and Lai, 2012). Che Man and co-workers (1999) studied the composition of crude palm oil (CPO) and its products. It was reported that the refined bleached deodorized (RBD) palm olein and superolein had a higher content of unsaturated fatty acid than crude palm oil (CPO), while the highest saturated fatty acid content is refined bleached deodorized (RBD) palm stearin. The fatty acid compositions and the various glyceride molecules are shown in Table 2.2 and Table 2.3, respectively.

Table 2.2 Fatty acid composition of palm oil and its products (Che Man *et* al., 1999)

	Fatty acid composition (%)				
Fatty acid	CPO[a]	RBD palm oil	RBD olein	RBD stearin	Superolein
Saturated					
M	0.93	0.92	0.89	1.21	0.81
P	45.48	46.30	41.54	61.21	38.47
S	3.49	3.52	3.51	4.00	3.14
Total	49.91	50.74	45.94	66.42	42.42
Unsaturated					
O	40.17	39.58	43.63	27.54	45.77
L	9.92	9.68	10.43	6.05	11.81
Total	50.09	49.26	54.06	33.59	57.58

[a]CPO, crude palm oil; RBD, refined, bleached, deodorized; M, myristic; P, palmitic; S, stearic; O, oleic; L, linoleic.

Table 2.3 Glyceride composition of palm oil and its products (Che Man *et* al., 1999)

	Glyceride composition (%)				
Fatty acid	CPO[a]	RBD palm oil	RBD olein	RBD stearin	superolein
Diglyceride	6.32	5.20	5.55	5.15	6.24
Triglyceride	93.60	94.80	94.45	94.85	93.76
Triunsaturated					
OOO	3.90	4.40	4.61	2.14	5.25
OOL	1.22	0.58	0.66	1.81	0.77
Total	5.12	4.98	5.27	3.95	6.02
Monosaturated					
PLO	10.02	9.68	10.63	4.53	12.56
POO	21.39	23.26	25.60	9.40	29.13
OOS	2.78	2.24	2.58	2.47	3.17
Total	34.1	35.18	38.81	16.40	44.68
Disaturated					
MPL	3.03	2.20	2.52	2.22	2.99
PPL	9.37	9.23	9.61	7.18	10.14
PPO	27.39	29.62	29.64	23.36	22.46
POS	5.29	4.90	5.11	3.85	3.97
SOS	1.36	-	0.68	-	0.51
Total	46.43	45.95	47.56	36.61	40.07
Trisaturated					
MMM	0.76	0.42	0.46	0.93	0.54
MMP	2.38	1.70	1.85	2.05	2.27
PPP	4.81	5.51	0.50	27.16	-
PPS	-	1.06	-	5.06	-
Total	7.95	8.69	2.81	35.20	2.81
Unknown	-	-	-	2.69	-

[a] See Table 2 for abbreviations.

Tanthakit *et al.* (2010) studied palm oil detergency at 30 °C by using a mixture of an anionic extended surfactant (branched $C_{14,\ 15}$-3PONaSO$_4$)/nonionic secondary alcohol surfactant under conditions corresponding to ultralow oil/water interfacial tension microemulsion formation. It was reported that the selected formulation of anionic/nonionic surfactant mixture at 25/75 weight ratio provided the highest oil removal compared with the single surfactant and the commercial liquid detergent.

The maximum palm oil removal for the selected formulation at 83%, corresponding to the minimum equilibrium or dynamic IFTs as shown in Figure 2.3. Moreover, the total oil removal increased with increasing NaCl concentration and it reached at 2 wt% NaCl. In addition, Tongcumpou *et al.* (2006) showed exceeding 80% oil removal with triolein using a mixture of anionic and nonionic surfactants with total surfactant active content of 2,500 ppm.

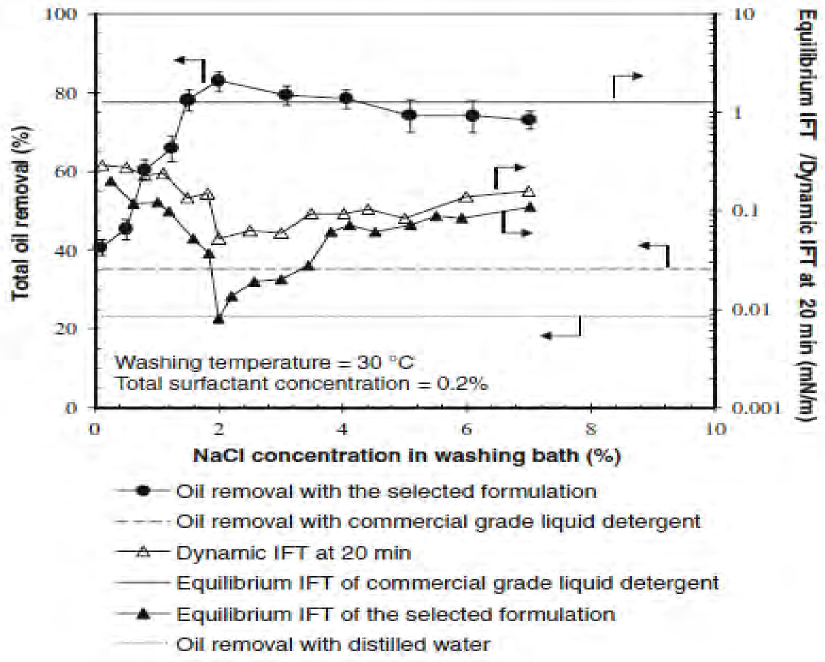


Figure 2.3 Oil removal, equilibrium IFT and dynamic IFT between washing solution and oil as a function of salinity with the selected formulation as compared to the commercial grade liquid detergent (Tanthakit, 2010).

2.4 Microemulsion

Microemulsions are a system consisting of oil, water and an amphiphile (surfactant and co-surfactant) in liquid state that having droplet sizes of 10-100 nm (0.01-0.1 μm). They are thermodynamically stable compositions and are formed spontaneously or with gentle mixing of the components is reached. Microemulsions can either be oil-in-water, water-in-oil or both (Rosen, 2004). The HLB (hydrophilic and lipophilic) value can predict the action of a surfactant. For example, surfactants having low HLB value (HLB<10) would be good for water-in-oil (W/O) microemulsion whereas surfactants having high HLB value (HLB>10) would be good for oil-in-water (O/W) microemuulsion (Gadhave, 2014). Microemulsions can be classified into four types which are shown in Figure 2.4.

Winsor type I: Oil-in-water (O/W) microemulsion is formed by solubilizing surfactant preferably in water phase with an excess oil phase.

Winsor type II: Water-in-oil (W/O) microemulsion is formed by solubilizing surfactant preferably in oil phase with an excess water phase.

Winsor type III: In this microemulsion, there are three phases, excess oil and water phases in equilibrium with a middle phase containing oil, water, and surfactant.

Winsor type IV: This microemulsion type is formed by increasing surfactant concentrations where the middle phase extends and becomes a single phase.

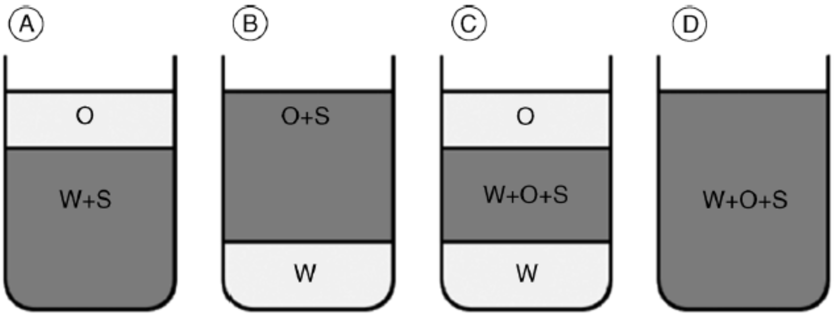


Figure 2.4 Winsor types classification of equilibrated emulsion with oil (O), water (W), and surfactants (S). A) Winsor type I; B) Winsor type II; C) Winsor type III; D) Winsor type IV (Matthia, 2015).

Fish diagram is the general pattern of microemulsion transition where the Winsor type I, II, and III microemulsion exist as shown in Figure 2.5. The total surfactant concentration (γ) plots with a tuning parameter (χ), which can be surfactant mixture, salt concentration (for ionic surfactants), or temperature (for nonionic surfactants). Winsor type IV system (single phase of oil, water, and surfactants) is formed with increasing the surfactant concentration and it is called a fishtail. The multiple phase systems are formed between Winsor type I, II, and III systems at minimum surfactant concentrations by tuning the χ parameter. So this generalized fish diagram is significant for the experimental interpretation and improvement of microemulsions (Matthia, 2015).

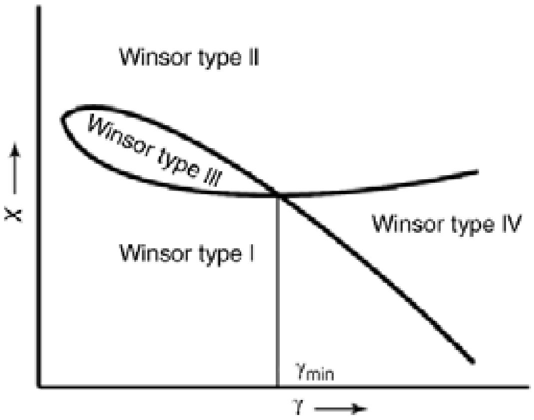


Figure 2.5 Generalized fish diagram for microemulsions (Matthia, 2015).

Do and co-workers (2015) studied the microemulsion phase behavior for vegetable oils (i.e., coconut and palm kernel oils) by using the mixture of a linear C_{10}-18PO-2EO-$NaSO_4$ extended surfactant and a hydrophobic twin-tailed sodium dioctyl sulfosuccinate (SDOSS) surfactant. They found that the middle phase microemulsions of coconut oil and palm kernel oil were observed at 1% and 1.5% NaCl, respectively. Moreover, the salt concentration relates to the microemulsion phase behaviors. For example, the phase behavior shows Winsor type I systems at low NaCl while Winsor type II systems occur at high NaCl.

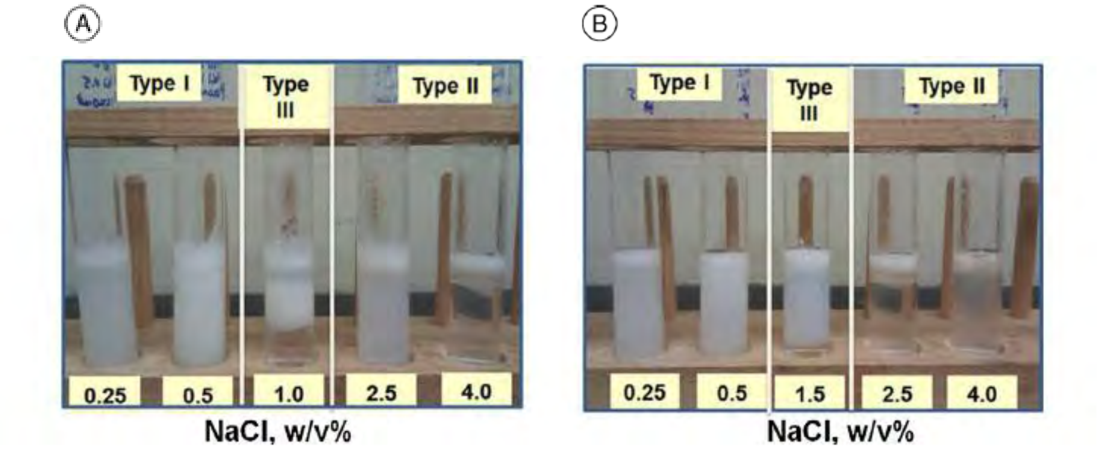


Figure 2.6 The experimental microemulsion phase behaviors. A) Coconut oil; B) Palm kernel oil versus NaCl scan (Do, 2015).

2.5 Cloud Point and Krafft Point

Cloud point and krafft point are the unique property of nonionic and anionic surfactants, respectively. At these points, the surfactant solubility becomes similar to the critical micelle concentration (CMC). The CMC is the property of the surfactant. This point indicates that the properties of surfactant are at an optimum. It means that the surfactant solution become turbid which separate the solution into two phases (Rosen, 2004). These properties are important to determine the storage stability of the surfactant solution. Moreover, the CMC is the significant property in order to select the surfactant for specific application such as surface tension, solubilisation, interfacial tension, electrical conductivity and turbidity (Farn, 2006).

2.6 Surfactant Adsorption

The surfactant adsorption on solid surface is commonly determined by the adsorption isotherms. This process can be determined the amounts of surfactant adsorbed onto a solid-liquid interface depend on these factors: 1) the solid surface (polarity, non-polarity and surface charge) 2) the molecular structure of the surfactant being adsorbed (charge of head group and hydrophobic tail properties) 3) the aqueous phase (pH, salinity concentration, additive and tempeerature) (Farn, 2006). Normally, Isotherm can be divided into four regions. This diagram plot in log-log scale with the equilibrium surfactant concentration and the amount of surfactant adsorbed on the surface. Figure 2.7 was observed for adsorption of ionic surfactant on oppositely charged solid surface and adsorption of nonionic surfactant on silica surface.

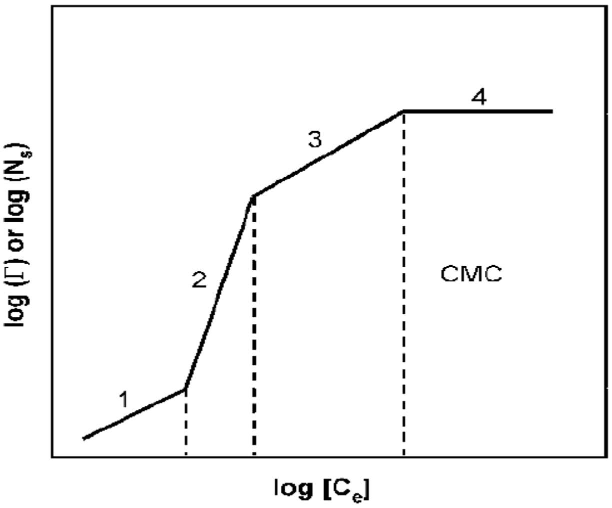


Figure 2.7 Four region isotherms of surfactant adsorption (Farn, 2006).

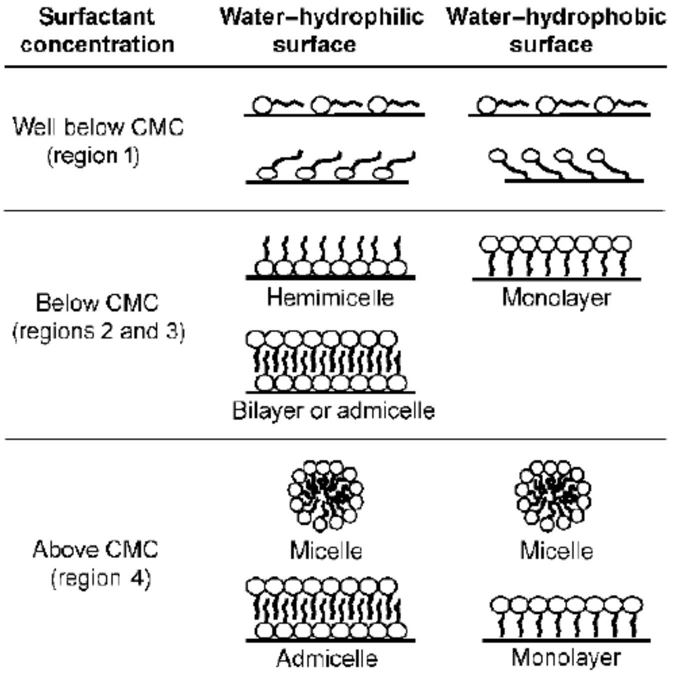


Figure 2.8 Surfactant adsorption on solid surfaces (Farn, 2006).

Region I: At this region, the concentration of adsorbed surfactant monomer is quite low. It can also be called Henry's law region which shows the slope of linear adsorption isotherm of 1. Therefore, the interactions between each surfactant ions do not occur and the zeta potential do not change on the solid surface. For nonionic surfactants, the mechanism of surfactant adsorption occurs from either the bonding of hydrophobic or the bonding of hydrophilic of solid surface. For anionic surfactants, the electrostatic interaction of hydrophilic or hydrophobic bond can cause the surfactant adsorption on the solid surface.

Region II: At this region, the adsorption isotherm is increased rapidly with a slope higher than 1 due to the formation of local monolayer (hemimicelles) or bilayer (admicelles) aggregates on the surface (Tabatabal, 1993). The break point between regions I and II is called the critical admicelle concentration (CAC) or hemimicelle concentration (HMC). This concentration is lower than that of CMC. Moreover, there are some residual spaces for further adsorption of surfactant and the surfactant adsorption with opposite charge neutralizes the solid surface charge.

Region III: In this region, the slope of adsorption isotherm shows a slower rate than region II. This is because of the lower the bilayer rate and less of surfactant adsorption on the solid surface.

Region IV: The formation of surfactant micelle completes with the surfactant adsorption causes the plateau in this region. This region, surfactant adsorption becomes nearly constant with increasing surfactant concentration (Tabatabal, 1993). CMC or critical micelle concentration occurs at the break point between regions III and IV.

2.6.1 Electrical Double Layer

The interface has unequal power distribution of electrical charges between the two phases. Therefore, it makes one interface side to get the net charge of a particular signal while the other side get the net charge of the reverse signal. It can cause the electrical double layer, leading to higher potential between the interfaces.

As the overall electrical neutrality must be maintained, the one side of net charge interface must be equalized by a reverse charge on the other side of the interface with an exactly equal amount (Rosen, 2004). The schematic of electrical double layer as shown in Figure 2.9.

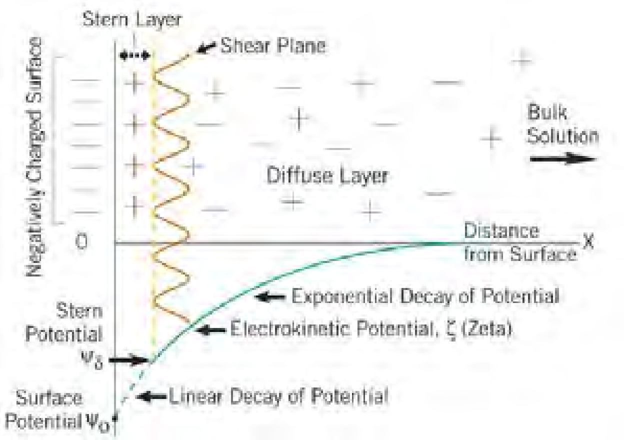


Figure 2.9 Schematic presentation of electrical double layer at a charged interface in aqueous solution.

2.6.2 Zeta Potential

The zeta potential magnitude represents the stability in the colloidal system, indicating to the repulsion force between the similarly charged particles in dispersion. The higher magnitude of both negative and positive zeta potentials, the higher repulsive force to each other. Then, they will no tendency for the particle to come together. In contrast, the lower the zeta potential of particles, the lower the repulsive force to prevent the particle coagulating, as shown in Figure 2.10.

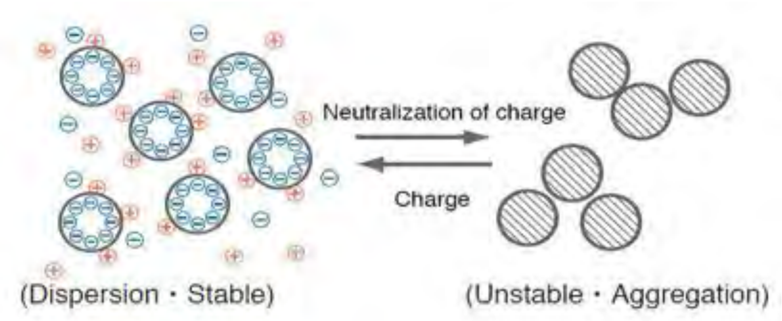


Figure 2.10 A dispersion stability of the particle disperses well and the particle aggregation.

Figure 2.11 shows the typical plots between the zeta potential (mV) and pH level of solution to determine the PZC. For the PZC higher than a solution pH, the surface has positive charge resulting in the preferable adsorption of anionic surfactants. For the PZC lower than a solution pH, the surface has negative charge resulting in the adsorption of cationic surfactants. The dividing line between stability and instability is usually used at +30 or -30 mV. In general, the particle with the magnitude of zeta potentials greater than +30 mV or lower than -30 mV are considered stable.

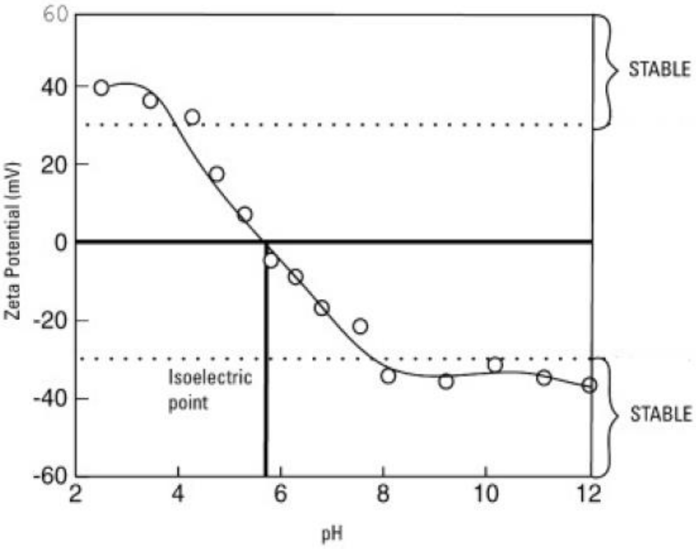


Figure 2.11 A plot of the zeta potential measured as a function of pH.

2.7 Mechanism of Oily Soil Removal

There are three major mechanisms of oily soil removal are as follows: roll-up or roll-back, emulsification or snap-off, and solubilization (Rosen, 2004).

2.7.1 Roll-up or Roll-back Mechanism

The roll-up or roll-back mechanism is the most important mechanism for oily soil removal. This is a complete removal of oily soil droplet from the surface of substrate in the presence of surfactant. There are two processes that can remove oil droplet. Firstly, an increasing contact angle between oily soil and substrate by adsorption of surfactant from the cleaning bath. Second, the occurrence of the repulsion force between the head group of surfactant.

2.7.1.1 The Increased Contact Angle Process

This process can be explained by Young's equation by the expression:

$$\cos\theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}}$$

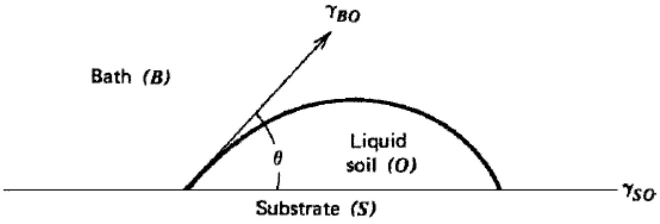


Figure 2.12 The contact angle between oil droplet and substrate in bath (Rosen, 2004).

When surfactants are presented in the bath (B) or surfactant solution, they will adsorb at two interfaces: 1) the interface between substrate and bath (SB) and 2) the interface between oily soil and bath (OB). As a result of increasing in θ or decreasing in cos θ, the reduction of interfacial tension (IFT) between substrate and bath (γ_{SB}) interface and that between oily soil and bath (γ_{OB}) interface is occurred. This situation can remove the oil droplet from substrate. However, this mechanism will be achieved when the contact angle is higher than 90°. The higher contact angle, the higher oily soil removal. When the contact angle is 180°, the oily soil will be completely removed from the surface of substrate. If the contact angle is between 90° and 180°, the hydraulic flow will aid the soil to remove in the bath as shown in Figure 2.13. When the contact angle is less than 90°, the soil will not be completely removed which there is some part of the oily soil remaining on the substrate. Therefore, some mechanism (solubilization) or mechanical action must be used to remove the residual oil from substrate (Rosen, 2004).

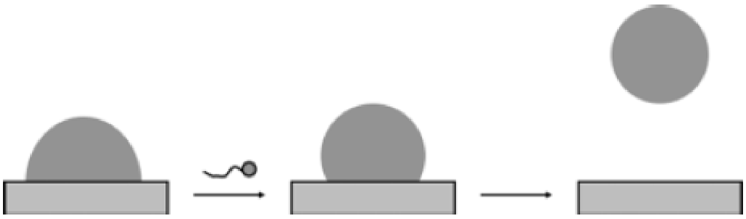


Figure 2.13 The roll-up mechanism shows the complete removal of oil droplet from the fabric θ > 90° (Kronberg, 2014).

2.7.1.2 Surfactant Head Group Repulsion Process

Adding the surfactants, they will adsorb at substrate-bath interface (SB) and oily-bath (OB) interface. Figure 2.14 shows each molecule of surfactant is represented by a shape pin while the hydrophilic group is represented by the solid circle as well as the hydrophobic group is represented by the straight line. The oily soil droplet is represented by the open circle. The head group of surfactants which adsorb at substrate-bath interface repulsing with the head group of surfactants which adsorb at oily soil-bath interface. According to the repulsion force, the oil droplet can be removed from the surface or substrate as shown in Figure 2.14.

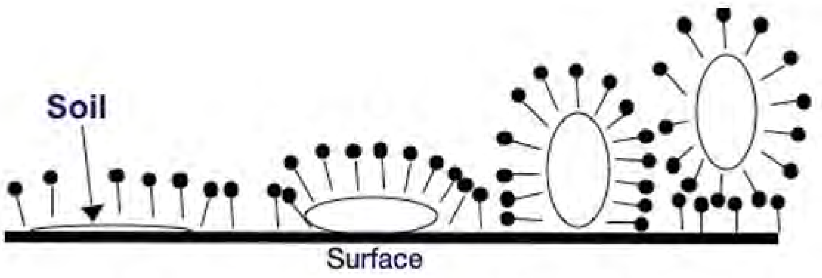


Figure 2.14 Repulsion force of surfactant head group.

2.7.2 Emulsification Mechanism or Snap-off

The emulsification or snap-off mechanism will occur when the contact angle between oil droplet and substrate less than 90°. The principle of this mechanism is same as a roll-up mechanism but the difference is the contact angle between the oil droplet and the substrate. Moreover, this mechanism is independent of the nature of the fabric (Kronberg, 2014). However, the disadvantage of this mechanism is some residual soil remaining on the substrate since the soil/bath interfacial tension is decreased, but the substrate/bath interfacial tension is not change substantially.

Figure 2.15 The emulsification mechanism shows partial removal of oil droplet from fabric θ < 90° (Kronberg, 2014).

2.7.3 Solubilization Mechanism

The solubilization process is oil adsorption inside the core of the surfactant micelles. There are several factors that affect the capacity of solubilized oil in the micelle such as temperature, electrolyte concentration, surfactant concentration, and the nature of oil and surfactant. The important roles of this mechanism are; 1) to removal a small amount of residual oil which cannot be removed by the roll-up or emulsification and 2) to prevent the oily soil from redeposition on the substrate. The solubilization will substantially occur when the surfactant concentration are above the critical micelle concentration (CMC) or form to micelles. At low surfactant concentration, the small amount of oil can be dissolved or solubilized in the solution. In contrast, the large amount of oily soil can adsorb in the micelle core which is similar to microemulsion formation at high concentration of surfactant (10-100 time CMC). The difference between the solubilization and emulsification mechanism is the thermodynamic stability to keep all the oily soil from redepositing on the substrate, whereas the emulsification mechanism cannot prevent the redeposition of the oily soil on the substrate. For the solubilization, it is not only important mechanism in the detergency process but also significant mechanism in polymerization, wastewater treatment, and separation of materials process.

Figure 2.16 The solubilization mechanism of oily soil removal from fabric (Kronberg, 2014).

2.8 Mechanism of Particulate Soil Removal

Particulate soils normally have a large specific surface area, so they are highly attractive surface interactions between particulates and fabrics along with the interaction between surfactant, fabric, soil, and agitation speed can affect the detergency process. They are difficult to remove because of their heterogeneous properties and water insolubility. Moreover, solid particles having a particle size below 0.2 µm cannot remove by water alone and tend to redeposit easily on the fabric.

Adding of ionic surfactant, the electrostatic repulsion of the particulate soil and the substrate is occurred. In addition, it can decrease either interfacial tension or adhesion force between particles. It is major mechanisms of enhancement of particulate soils removal by ionic surfactants. After anionic surfactants are added and then the surface becomes a negative charge. The particles will be removed by electrostatic repulsion and suspend in the solution as shown in Figure 2.17.

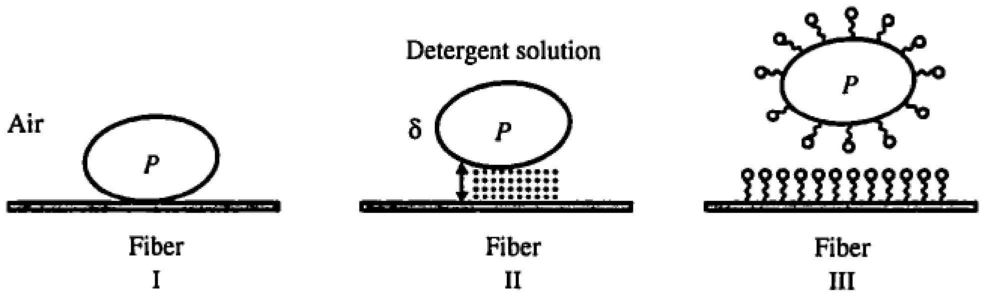


Figure 2.17 Particle soil removal.

2.9 Detergency

Detergency is the removal of unwanted materials or soils from substrate with an aid of surfactant. The surfactant provides the specific cleaning action by lowering the interfacial surface tensions, emulsification, solubilization as well as charge modification in cleaning process in order to remove soils and prevent the re-deposition of soils. In the study of detergency formulation and performance, there are many factors such as temperature, washing time, agitation speed, surfactant concentration, surfactant formulation, nature of soil, water hardness, electrolyte concentration and the order of application should be considered (Webb, 1988). The factors affecting oily soil removal are as follows:

2.9.1 Surfactant System

Many studies have reported that the performance of detergency corresponds to the surfactant system. For nonionic surfactant, the maximum detergency efficiency corresponded to the phase inversion temperature or PIT where a minimum of oil-water interfacial tensions is occurred. Moreover, the optimum temperature was increased as the degree of ethoxylation of the nonionic surfactant increased (Solan, 1988 and Tongcumpou, 2003). The oily soil removal was affected by the ethoxylation numbers in nonionic surfactant. The more ethoxylation numbers of the C_{12-14} alkylpolyglycol ether was increased, the less solubilization power of surfactant decreased which resulting the decrease in oily soil removal.

For anionic surfactant, electrolyte concentration or salinity is usually used to achieve the optimal points at optimum salinity (S*) in the Winsor type III region. In addition to, anionic surfactant is effective to remove oil from polar fabric. However, there was little or no difference between two types of surfactants in oily soil removal from the polyester/cotton fabric.

In general, the mixed surfactant is widely used in many applications especially in the areas of detergency. The mixed surfactant of anionic and nonionic surfactants perform better than the single surfactant. Moreover, they can also produce the microemulsions with enhancing the solubilization and ultralow interfacial tension (Poorgholami-Bejarpasi, 2010).

Tongcumpou *et al.* (2003) investigated the phase behavior of mixed surfactant system with highly hydrophobic oil of hexadecane and motor oil. These mixed surfactant can balance the hydrophilic and lipophilic part between water/oil phase. The surfactants that used in their study are as follows: alkyl diphenyl oxide disulfonate (ADPODS, highly hydrophilic), dioctyl sodium sulfosuccinate (AOT, intermediate character), sorbitan monooleate (Span 80, highly hydrophobic). They found that the minimum interfacial tensions do not lead to achieve a middle phase microemulsion. In addition, Winsor type III microemulsion can achieve with the varying HLB values of mixed surfactant. For the optimal middle-phase systems, the salinity required is quite high (5% NaCl) that is not practical for real application. In 2005, Tongcumpou also found that the removal of oily soil in the rinse step was as high as in wash step for both sopersolubilization and Winsor type III region. Because the spreading effect can occur at the wash step.

In 2004, Korphol *et al.* discovered the mixed surfactant system of 1.5 wt% ADPODS, 5 wt% AOT, and 5 wt% Span 80 can achieve a Winsor type III microemulsion at salinity of 2.83%. Furthermore, the detergency slightly increased with increasing the surfactant concentration. Moreover, the highest oil removal achieved at 0.1% of active surfactant concentration.

2.9.2 Nature of Oil

In 1963, Scott found that the presence of polar oil can increase nonpolar oil removal. Squalene was difficult to remove when it presents as a single soil more than when it was in a mixing oil. Furthermore, the mixing effect on the squalene removal is invesred after aging. Moreover, the viscosity of oil influenced the oil removal (Kissa, 1987). The lower viscosity of oil, the more oil removal from substrate when compared with the higher viscosity.

Raney and Benson (1990) investigated the effect of polar soil components on the phase inversion temperature as well as the optimum conditions of detergency. They found that the snap-off mechanism was resulted from the interfacial tension reduction at the soil and water interface that affecting nonpolar/polar soil mixtures removal. In addition, it was also suggested that a minimum quantity of polar material in the soil may be important to higher soil removal.

Chi *et al.* (2001) found that highly unsaturated oily soil was easily oxidize upon aging resulting in enhancing oil removal whereas saturated oils is stable. Moreover, aging can made oils to penetrate into the structure of substrate resulting in more difficult to remove.

2.9.3 Salt

Detergency performance with and without electrolytes as an effect of temperature was observed by Azemar *et al.* (1993). They used hexadecane as a model oily soil and polyester/cotton fabrics in their experiment. They found that detergency efficiency both with and without electrolyte followed the same trends with temperature in the systems. Moreover, this system is obtained the optimum when the temperature increased. Interestingly, there is a shift in the lower temperatures when the electrolyte concentration increase.

2.9.4 Substrate

The efficiency of soils removal depends upon type of the substrate. Morris and co-worker (1982) investigated the soil removal with different formulations from polyester, cotton, and cotton/polyester blend fabrics. They found that both particulate and oily soils were easier to remove from the cotton or polyester/cotton blend than from polyester fabrics. In addition, the affinity of clay particles prefer the polyester fabric than the other fabrics since the polyester fabric carried more clay during soil application.

In 2001, Chi *et al.* investigated the effect of the substrate on the squalene removal (a nonpolar hydrocarbon). This oily soil is difficult to remove from a nonpolar substrate (polyester). In contrast, a polar substrate (cotton) may be expected to remove oily soil quite well compared with polyester in an aqueous detergent system. On the other hand, they found that a squalene removal on cotton fabric decreased since the morphological characteristics of cotton made oil difficult to be removed.

2.9.5 Water Hardness

The divalent cations calcium and magnesium in water are the important factor of water hardness. The detergency performance is affected by hard water in many negative effect such as color change of fabrics, damaged fabrics, and higher amount of detergent.

In 2009, Tanthakit *et al.* investigated the water hardness of motor oil with a microemulsion-based formulation. They found that the mixed surfactant formation of two parts $C_{14\text{-}15}(PO)_3SO_4Na$, and 98 parts $C_{12\text{-}14}H_{25\text{-}29}O(EO)_5H$ at 4% salinity can provide the Winsor Type III microemulsion. In addition, this system provided better detergency performance when compared with a commercial liquid detergent at 0.5% actives concentrations or less. The result shown that motor oil was removed more than 80%. However, both of the total oily soil removal and the interfacial tension slightly decreased in the presence of water hardness in the system. In general, the higher amount of oily soil removal achieved in the rinse steps. However, the oily soil removal in the rinse steps was decreased by increasing water hardness.

2.9.6 Other Factors

Linfield *et al.* (1962) investigated the detergency performance and formulation. It was found that an increasing of washing time, agitation speed and surfactant concentration resulted in increasing the efficiency of detergency to the maximum points. They observed that the agitation speed of 150-170 rpm as well as washing time at 15-20 min can provide the maximum detergency.

In 1982, Obendorf *et al.* reported that both mechanical action and detergent concentration can affect the soil removal. In their research, a residual triolein on cotton and polyester/cotton blend fabrics was studied. They found that an increase of either detergent concentration or mechanical action resulted in increasing of triolein removal. However, the cotton fabrics remained higher triolein than polyester/cotton fabrics.

Moreover, Raney *et al.* (1987) investigated the relationship of PIT with detergency performance. They found that the maximum detergency in the ternary systems that composed of water, surfactant, and soil at the phase inversion temperature (PIT). In another influencing factor, Webb et al. (1988) studied the different detergent formulations including an unbuilt liquid and powered detergents with various builder systems. They observed that soil removal by the built powdered formulation was higher than the unbuilt liquid formulation.

CHAPTER III
EXPERIMENTAL

3.1 Materials

Kaolinite (purum) was purchased from Sigma-Aldrich. Palm oil (Palm olein, Oleen) was obtained from OLEEN Company Limited, Thailand. The studied fabric was a standard unsoiled polyester/cotton blend (65/35), and was purchased from the Test Fabrics Co. (Middlesex, NJ, USA). The surfactants used were linear alkyl benzene sulfonate (LAS, technical grade) and sodium dodecyl sulfate (SDS, 99% purity) which were purchased from Sigma-Aldrich. Alcohol ethoxylate with seven and nine ethoxyl groups (AE7 and AE9, 99% purity) were purchased from Thai Ethoxylate Co., Ltd. Methyl ester sulfonated (MES, 99 % purity) were obtained from Lion Co., Ltd. Commercial liquid detergent (CM) contains 7.91% sodium linear alkylbenzene sulfonate, 1.85% ethoxylate alcohol, and 9.25% sodium lauryl ether sulfate (19.01% total surfactant concentration) as reported by the manufacturer. Analytical grade sodium chloride, Hydrofluoric acid (HF, analytical purity grade), nitric acid (HNO_3, analytical purity grade), dichloromethane (99% purity) and 2-propanol were purchased from the Lab Scan Asia Co. Ltd. Oil red O (solvent Red 27, CI. No. 26125) was purchased from the Aldrich Chemical Company, Inc.

3.2 Experimental Procedures

3.2.1 Detergency Performance

3.2.1.1 Fabric Pretreatment and Soiling Procedure

In this study, the soiling procedures were divided into two parts by following the different of soiling step.

Firstly, the test fabric (polyester/cotton blend) was pre-washed with distilled water to remove the residues of mill-finishing agents and cut into 5×5 cm in a wrap and weft direction. Then, the prepared test fabrics were first soiled with 0.5 wt. % of kaolinite by soaking into an aqueous soil solution. The mixing solution was suspended homogeneously by using a tergotometer (Copley, DIS8000) for 20 min. Then, the soiled fabrics were dried at room temperature overnight. The palm oil was dyed by the oil soluble Oil-red-O dye before applying it to the fabric. Approximately 0.1 g of the oil-soluble dye was added to 100 mL of palm oil. The colored oil was filtered until clear. The soiling procedure was done by diluting 1 mL of the clear dyed oil with dichloromethane to 5 mL. After that, the soiled fabric was then added with 1 mL of the dyed palm oil solution. The soiled fabric was laid on a flat plate in a ventilated hood at room temperature overnight.

3.2.1.2 Laundry Procedure

A tergotometer was used in this study as a standard testing unit for washing process. Four soiled fabrics and two unsoiled fabrics for anti-redeposition were added into each bucket. The testing system used was 1,000 mL of washing solution, 20 min washing, 3 min first rinse, and 2 min second rinse with de-ionized water. The temperatures of both washing solution and rinse water were set at 30 °C. This experiments were proceeded with washing solutions having different concentrations of anionic surfactants, nonionic surfactants, and a selected formulation. In addition, a commercial liquid detergent was used for comparison by following the similar procedure as mentioned above.

3.3 Measurement and Analysis Methods

3.3.1 CMC Determination

An aqueous surfactant solution with different weight fraction of anionic and nonionic surfactants was prepared at different total surfactant concentration. The surface tension measurement was evaluated by using a tensiometer (Kruss, EasyDyne) with the Wilhelmy Plate method. The plot of surface tension vs. the log of surfactant concentration can indicate the critical micelle concentration (CMC) of surfactant.

3.3.2 Detergency Performance Evaluation

The detergency performance was evaluated by reflectance method of pre-washed and post-washed fabrics. The reflectance measurement was conducted by a colorimetric spectrophotometer (Hunter Lab, Color Flex). The reported L parameter of this instrument is representative of the brightness of the fabric. The maximum value of L is 100 (completely white) and the minimum for L is zero (completely black). A decrease in L parameter represents an increase in darkness of test fabric. The detergency performance was calculated in terms of the percentage of detergency (%D) by using the following equation:

$$\%D = \text{Detergency}(\%) = [(A - B) \div (C - B)] \times 100$$

Where A is the average reflectance of the soiled fabrics after washing. B is the average reflectance of the soiled fabrics before washing and C is the average reflectance of the unsoiled fabrics before washing.

3.3.3 Oil Removal Measurement

For measurement of oil removal, the attached oil on the test fabrics before and after the laundry experiment was extracted from the fabric sample by submerging the fabrics in 2-propanol with 2 times overnight at room temperature. The amount of extracted oil in the solution was measured by using a UV/VIS spectrophotometer (Shimadzu, UV-1800).

3.3.4 Dynamic Interfacial Tension (IFT) Measurements

The measurement of Dynamic IFT of solutions containing different surfactant concentrations of AE, MES, LAS, and SDS was conducted by using a spinning drop tensiometer. The heavy phase of surfactant mixture was the washing solution and the light oil phase was the dyed palm oil. A volumetric ratio of aqueous solution-to-oil of 100:1 was used to measure interfacial tension. The diameter of the oil drop was measured after 20 min as the rotational velocity was kept constant.

3.3.5 Silica Analysis

For particulate soil removal, the soil fabric samples before and after the washing experiment were digested with concentrated hydrofluoric acid and nitric acid to dissolve the kaolinite. After the digestion step, the mixture was filtrated and diluted with deionized water. The concentrations of silicon (Si) for the kaolinite was analyzed by using atomic absorption spectroscopy (Varian, SpectrAA300) at a wavelength of 251.6 nm for Si.

3.3.6 Zeta Potential Measurement

Each of studied solid sample was added into a surfactant solution and then the mixture was stirred at 30 °C for 24 hours. After that the solution was transferred to an electrophoretic cell of a zeta meter (Zeta Meter 3.0+ unit) equipped with a microscope module. After applying a suitable voltage, the charged particles move towards to the electrode until attaining a steady state (the particle move with a constant velocity). The velocity was then measured and referred as its electrophoretic mobility, which automatically calculates the zeta potential in millivolt unit by using the Helmhotlz-Smoluchowski equation. For a given data set, at least 20 particles were monitored and the average zeta potential value was reported.

3.3.7 Point of Zero Charge (PZC) Measurement

The sample were added into deionized water having different pH solution. The solution pH was adjusted by using a 1 M HCl or 1 M NaOH solution. The solution was then stirred at 30 °C for 24 hours. After that, the initial and the final pH value of this solution were measured with the pH meter (Ultra basic DENVER

Instrument). PZC could be found from the plot between final pH in y-axis and initial pH in x-axis, the pH that no change in the initial and final pH was reported as the PZC of those samples.

CHAPTER IV
RESULTS AND DISCUSSION

In this part, the detergency of mixed soils between particulate soil and oily soil from polyester/cotton blend fabric are investigated at constant washing temperature, 30 °C. In addition, the basic properties of studied surfactant such as critical micelle concentration (CMC), dynamic interfacial tension (IFT) and zeta potential are determined to relate with the detergency performance.

4.1. Critical Micelle Concentration (CMC)

The critical micelle concentration (CMC) is defined as the minimum surfactant concentration that the first micelle is formed. The CMC of studied surfactant is obtained from the break-point plateau in the plot of surface tension versus logarithm surfactant concentration as shown in Figure 4.1. The results show that the CMC of all studied surfactants which are alcohol ethoxylate 7EO (AE7), alcohol ethoxylate 9EO (AE9), methyl ester sulfonate (MES), linear alkyl benzene sulfonate (LAS) and sodium dodecyl sulfate (SDS) are 89 µM, 92 µM, 1,900 µM, 2,500 µM and 8,000 µM, respectively. The CMC results of studied surfactants are in good agreement with those reported in the reference (Rosen, 2004). However, the obtained CMC value of MES is quite different possibly due to the differences of hydrophobic tail length and experimental temperature between this study and the reference.

For nonionic surfactants (AE7 and AE9), the CMC of the two surfactants are lower than the CMC of anionic surfactants (MES, LAS and SDS) as observed in the other reports (Rosen, 2004). As a result, the nonionic surfactants can form micelle easily and should provide good detergency efficiency at low surfactant concentration (Rosen, 2004).

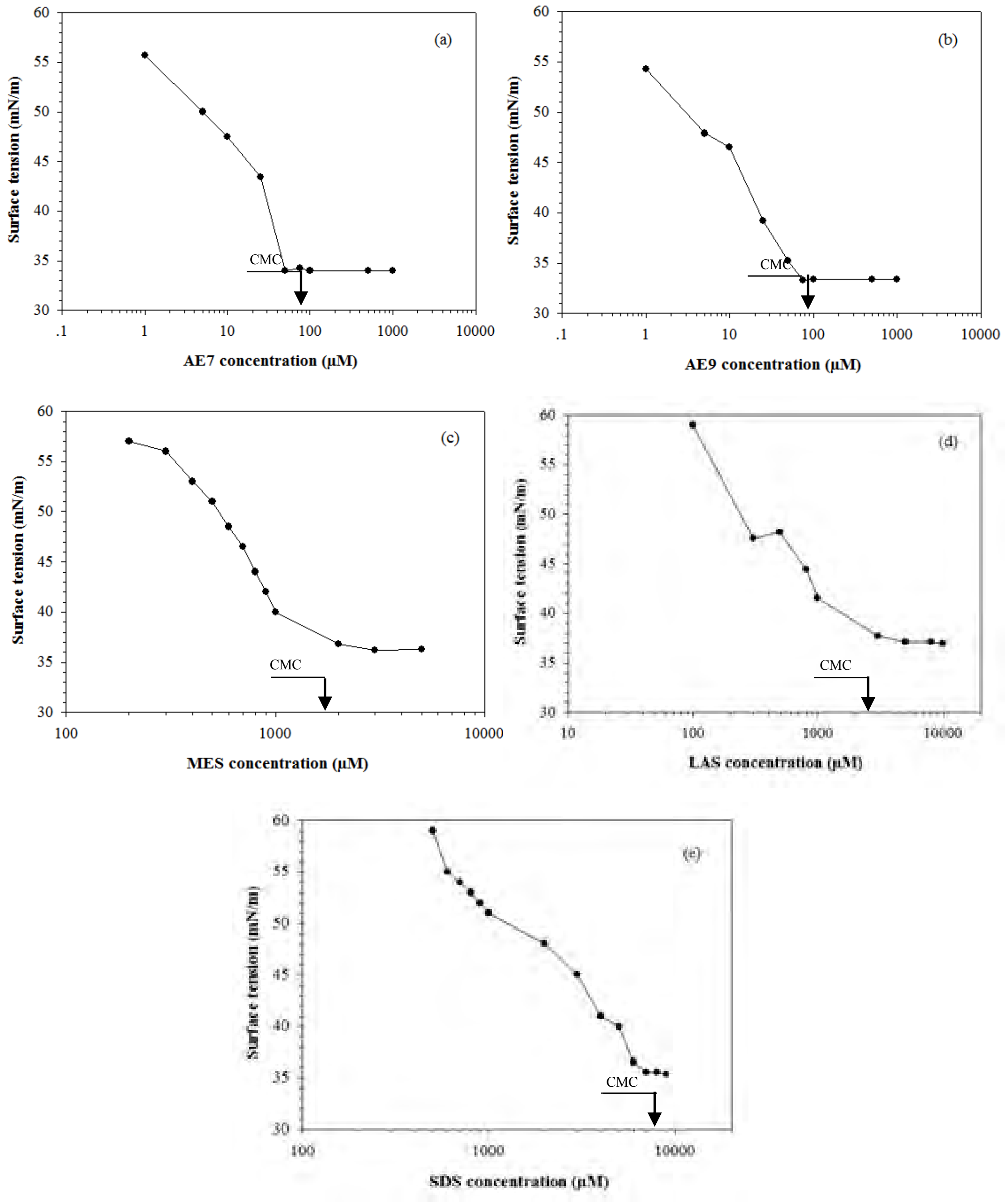


Figure 4.1 Plot of surface tension versus surfactant concentration of (a) AE7, (b) AE9, (c) MES, (d) LAS, and (e) SDS at 30 °C.

4.2 Detergency Performance

4.2.1 Single Surfactant System

4.2.1.1 Correlation between Dynamic Interfacial Tension (IFT) and Detergency of Oil on Fabric

Figure 4.2 presents the surfactant concentration on detergency performance and dynamic IFT at 20 min of different studied surfactants (AE7, AE9, MES, LAS and SDS) at various concentrations (0.05 wt. %, 0.1 wt. %, 0.2 wt. %, 0.3 wt. %, 0.4 wt. %, 0.5 wt. %, 0.6 wt. % and 1 wt. %) at 30 °C. As observed in the studied surfactant systems, the detergency efficiency increases with increasing total surfactant concentration and reaches plateau at certain surfactant concentration, depending on the washing condition such as nature of surfactant, fabric, and soils (Webb, 1988). Among the studied surfactant systems, LAS provides the highest detergency with efficiency at 61.4% and reaches the plateau at around 0.3 wt. % of total surfactant concentration. At this concentration, the results for detergency of AE7, AE9, MES, SDS and the commercial liquid detergent (CM) are 58.4%, 50.9%, 36.4%, 58.2% and 50.9%, respectively. Figure 4.2 also shows the dynamic IFT of all studied surfactant systems as a function of surfactant concentration at 30 °C. The IFT of the studied surfactant solutions are measured at 20 min, which is long enough for equilibrium and correlates to the detergency experiment (Attaphong, 2017). The results show that the IFT of all studied surfactant solutions well below 0.1 mN/m which are considered to be low enough for detergency application (Tongcumpou, 2003), compares with 0 wt. % surfactant concentration (approximate 9 mN/m). Interestingly, LAS provides the lowest IFT which also produces the better detergency performance.

The total oil removal results are determined from the amount of oily soil residue on fabric after washing procedure. Figure 4.3 illustrates the dynamic IFT at 20 min with the percentage of oil removal and oil re-deposition on fabric as a function of total surfactant concentration. As expected, the total oil removal increases with increasing the total surfactant concentration since an increase in the total surfactant concentration simply increases the micelle concentration, leading to higher oil solubilization (Rosen, 2004). The oil removal reaches the plateau at around

0.3 wt. % of total surfactant concentration. At this concentration, the results for total oil removal of AE7, AE9, MES, LAS, SDS and CM are 73.5%, 73.9%, 38.5%, 80.3%, 68.4% and 55.9%, respectively. For anionic surfactant systems, the highest oil removal is LAS which corresponds to the lower dynamic IFT. For nonionic surfactant (AE7 and AE9) systems, the percentages of oil removal of AE7 and AE9 are insignificant with efficiency 73.5% and 73.9%, respectively. Therefore, both anionic surfactant (LAS) and nonionic surfactants (AE7 and AE9) should be mixed and used for further detergency experiment.

The oil re-deposition on fabric results are calculated from the differences in the amount of oil on pre and post washed of unsoiled fabric. For the absence of the studied surfactants, it is obvious that the oil re-deposition on fabric is higher than the system in all the surfactant solution as shown in Figure 4.3.The re-deposition decreases with increasing the total surfactant concentration and reaches the minimum when increasing surfactant concentration greater than 1 wt. % for all the studied surfactant.

4.2.1.2 Correlation between Particulate Soil Removal and Particulate Soil Re-deposition on Fabric

The particulate soil removal are indicated from the differences of the amount of silicon concentration on pre and post washed soiled fabrics. Figure 4.4 shows the particulate soil removal and re-deposition on fabric as a function of total surfactant concentration. The results show the particulate soil removal gradually increases with increasing the total surfactant concentration in all the studied surfactant systems since the higher total surfactant concentration, the higher surfactant adsorption on both surfaces of fabric and particulate soil (Paria, 2004). This is attributed to the repulsion forces between the soil particle and fabric surfaces. It reaches the plateau at around 0.3 wt**.** **%** of total surfactant concentration. At this concentration, the results for particulate soil removal of AE7, AE9, MES, LAS, SDS and CM are 62.6%, 66.8%, 45.2%, 67.7%, 52.6% and 74.9%, respectively.

Among all studied surfactant systems, the commercial liquid detergent provides the highest percentage of particulate soil removal. This results can be explained by the fact that the commercial liquid detergent contains a higher amount of anionic surfactant (LAS and SDS) and mixes with the nonionic surfactant (AE) which is good for particulate removal. This is probably due to the synergism of anionic surfactant and nonionic surfactant in the commercial liquid detergent formulation is better for particulate removal from fabric that can form mixed micelle and effective in soil removal (Verma, 1998). It is not surprising that the detergent with mixed surfactant systems are found to provide the highest particulate soil removal which will be discussed further with the mixed surfactant systems of the studied surfactant.

The results of particulate soil re-deposition on fabric are calculated from the differences in the amount of particulate soil on pre and post washed of unsoiled fabric. The particulate soil re-deposition decreases with increasing the total surfactant concentration as shown in Figure 4.4 because the higher total surfactant concentration, the higher electrostatic repulsion for anionic surfactants and stearic hindrance for nonionic surfactants on both surfaces of fabric and particulate soil (Rosen, 2004). However, the particulate soil re-deposition on fabric is less than 1% at all the studied surfactant. It is interesting to note that the percentage of particulate soil re-deposition is higher than that of the oil re-deposition since the particulate soils are not water soluble so they can be tend to redeposit back onto the fabric.

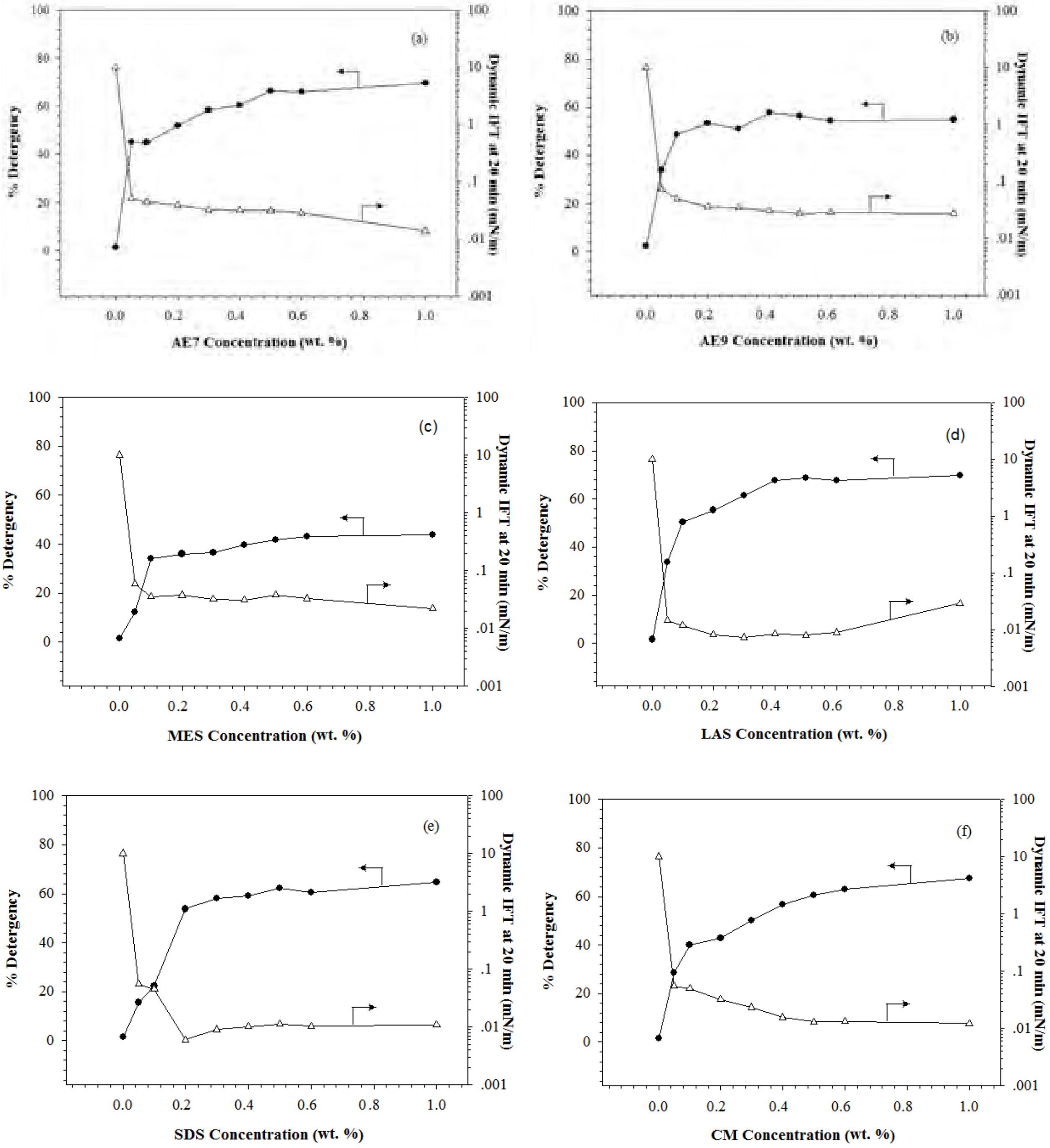


Figure 4.2 Detergency and dynamic IFT between oil and washing solution with the surfactant concentration of (a) AE7, (b) AE9, (c) MES, (d) LAS, (e) SDS, and (f) CM at 30 °C.

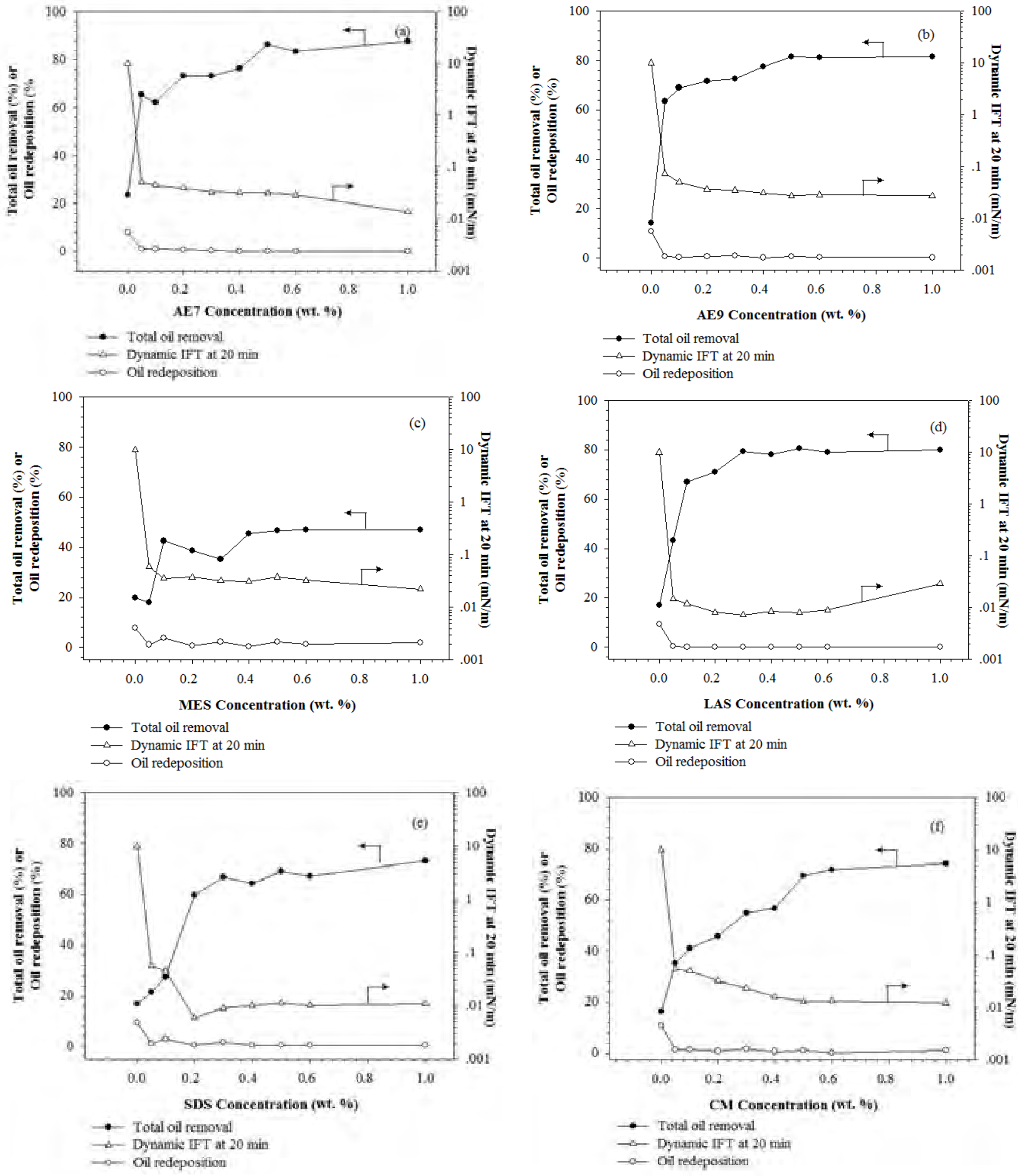


Figure 4.3 Total oil removal, oil re-deposition on fabric and dynamic IFT with the surfactant concentration of (a) AE7, (b) AE9, (c) MES, (d) LAS, (e) SDS, and (f) CM at 30 °C.

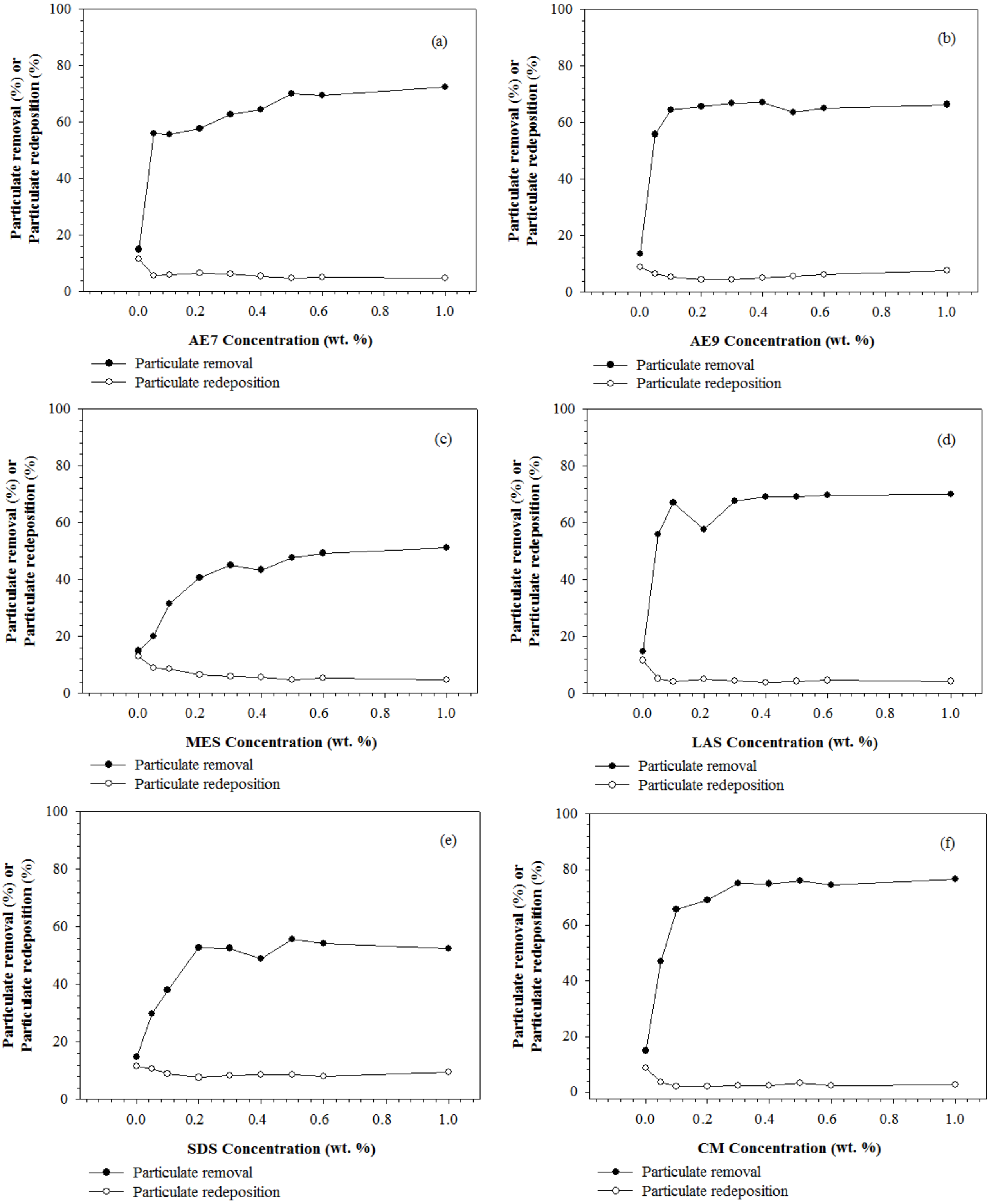


Figure 4.4 Particulate soil removal and particulate soil re-deposition on fabric with the surfactant concentration of (a) AE7, (b) AE9, (c) MES, (d) LAS, (e) SDS, and (f) CM at 30 °C.

4.2.2 Effect of Salinity on Detergency Performance

4.2.2.1 Correlation between Dynamic Interfacial Tension (IFT) and Detergency of Oil on Fabric

Salinity is an important parameter that affects to the detergency performance, especially for an anionic surfactant. Therefore, the detergency of AE7, AE9, and LAS is further investigated as a function of NaCl concentration at 0.3 wt. % of total surfactant concentration and a washing temperature at 30 °C as shown in Figure 4.5. The results show that the detergency slightly increases with increasing salinity for both nonionic surfactants (AE7 and AE9) with efficiency in the range of 60- 80 % and 50- 80 % for AE7 and AE9, respectively. For anionic surfactant (LAS), the detergency increases when increasing NaCl concentration from 0- 2 wt. % and reaches the maximum at 2 wt. % NaCl. However, the detergency decreases substantially when increasing NaCl concentration beyond 2 wt. %. Figure 4.5 also presents the IFT values of the studied surfactants. The results show that the IFT of AE7 and AE9 slightly decreases with increasing NaCl concentration which is shown an opposite trend to that of the detergency. Whereas the IFT of LAS significantly increases with increasing NaCl concentration beyond 2 wt. %. The addition of NaCl concentration causes the reduction of repulsive force between the surfactant head group by the Na^+ counter ion effect, leading to enhance the surfactant adsorption (Rosen, 2004). As a result, the lower IFT, the higher detergency performance.

Figure 4.6 shows the correlation between the percentage of oil removal and the dynamic IFT at 30 °C. The results show a similar trend of detergency but the different values since the percentage of detergency is qualitative measurement while the percentage of oil removal is quantitative measurement. Interestingly, the oil removal of all studied surfactants can achieve the percentage more than 80 % with added NaCl concentration, which corresponding to the minimum IFT. Among the studied surfactant systems, the oil removal of AE7 is higher than that of AE9. Hence, AE7 (nonionic surfactant) and LAS (anionic surfactant) should be used for further detergency experiment to study the mixed surfactant system.

For oil re-deposition of all studied surfactant system is lower than 1% at all range of salinity and did not change with increasing NaCl concentration as shown in Figure 4.6.

4.2.2.2 Correlation between Particulate Soil Removal and Particulate Soil Re-deposition on Fabric

Figure 4.7 shows the particulate soil removal and particulate soil re-deposition on fabric as a function of salinity at 0.3 wt. % of total surfactant concentration and 30 °C. The particulate soil removal and particulate soil re-deposition did not change substantially with increasing the salinity since the main mechanism of particulate removal is electrostatic repulsion for anionic surfactant systems and the steric stabilization for nonionic surfactant systems (Kronberg, 2014).

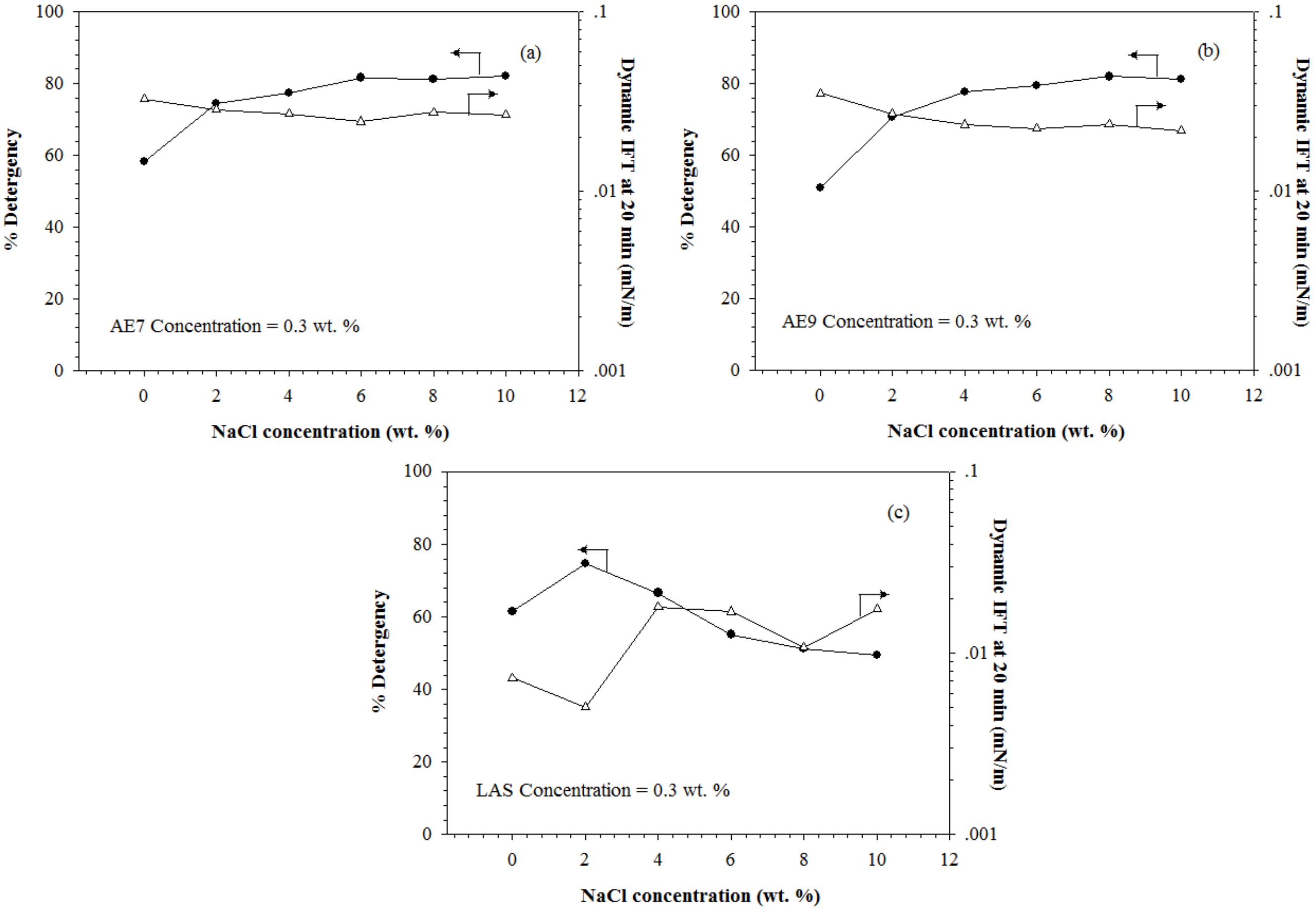


Figure 4.5 Detergency and dynamic IFT between oil and washing solution with the surfactant concentration of (a) AE7, (b) AE9, and (c) LAS as a function of salinity at 30 °C.

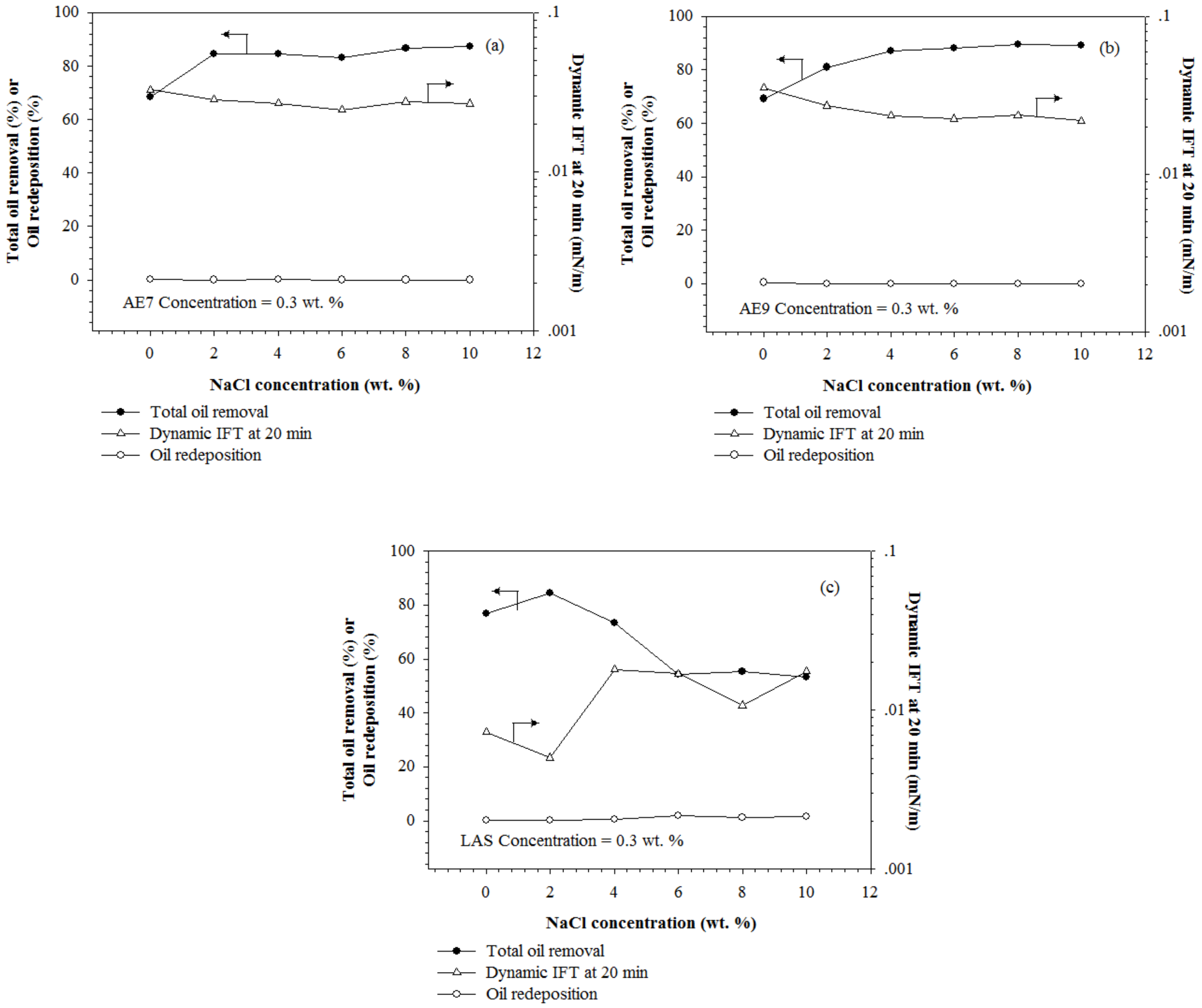


Figure 4.6 Total oil removal, oil re-deposition on fabric and dynamic IFT with the surfactant concentration of (a) AE7, (b) AE9, and (c) LAS as a function of salinity at 30 °C.

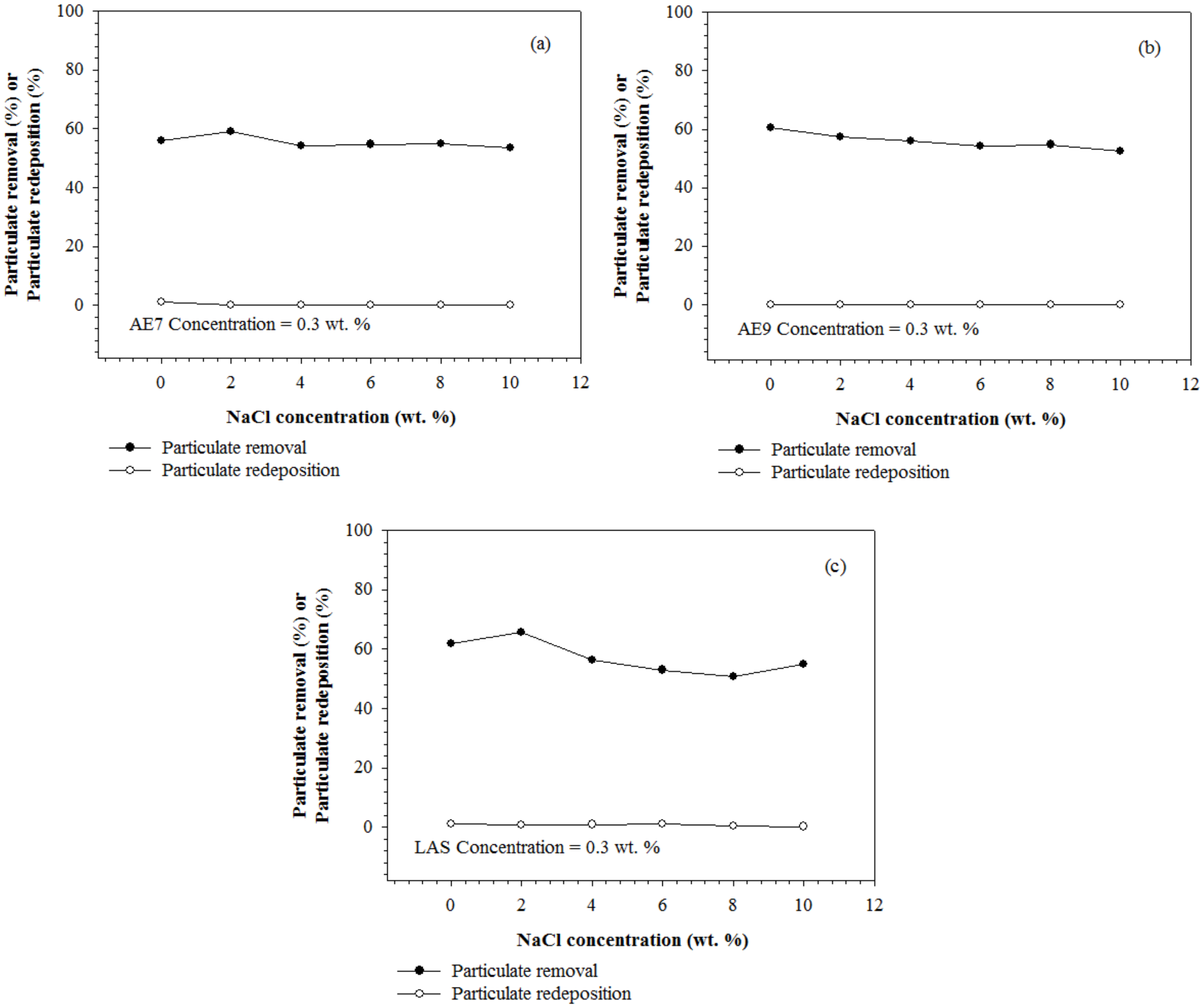


Figure 4.7 Particulate soil removal and particulate soil re-deposition on fabric with the surfactant concentration of (a) AE7, (b) AE9, and (c) LAS as a function of salinity at 30 °C.

4.2.3 Mixed Surfactant System on Detergency Performance

4.2.3.1 The Selected Surfactant Concentration on Detergency of Oil Removal and Particulate Removal on Fabric

Since both the anionic surfactant and the nonionic surfactant providing the highest detergency are LAS and AE7, respectively. So, mixed surfactant systems between LAS and AE7 should be focused on for better improving detergency. Hence, Figure 4.8- 4.10 present the detergency of mixed surfactant efficiency between

AE7 and LAS in the ratio of 1: 3, 1: 1, and 3: 1, respectively. The total surfactant concentration is fixed at 0.3 wt. % with 2 wt. % NaCl at 30 °C.

Figure 4.8 and 4.9 present the detergency, total oil removal and oil re-deposition on fabric. Interestingly, for any given different weight ratio of mixed surfactant systems, there are few significant differences found among the detergency result, the total oil removal and oil re-deposition on fabric compare with the results of single surfactant systems with the presence of 2 wt. % NaCl. The highest detergency is 74.4% of 3: 1 of AE7: LAS. For the highest total oil removal is found at the same weight ratio of 3:1 of AE7: LAS at 87.6%. Therefore, the detergency, the total oil removal and the oil re-deposition on fabric are not observed to be an important factor to detergency trends with the system of mixed surfactant. Figure 4.8 and 4.9 also present the IFT of the mixed surfactant systems. The results show that the IFT of mixed surfactant slightly decrease with increasing LAS concentration. Whereas the percentages of detergency and total oil removal are not significantly changed with any mixing surfactant ratio. However, the dynamic IFT of mixed surfactant systems could not be lowered below those of the pure LAS anionic surfactant alone.

Figure 4.10 shows the particulate removal and particulate re-deposition on fabric. The largest improvement of the particulate removal in the presence of mixed surfactant systems as compare with single surfactant systems is investigated. The mixed surfactant systems of 1: 3 of AE7: LAS provides the highest of particulate removal at 86.0%. As the result, it is clearly seen that the particulate removal of mixed surfactant systems of AE7 and LAS are better than the results of single surfactant systems. Because of the synergistic effect between the ethoxylated head group of AE7 and sulfonate head groups of LAS that blankets the electrostatic repulsion, leading to lowering the free energy of the system and favoring the formation of micelles (Sahu, 2015). It is not surprising that the particulate re-deposition on fabric always lower at all range of different weight ratio of mixed surfactant systems.

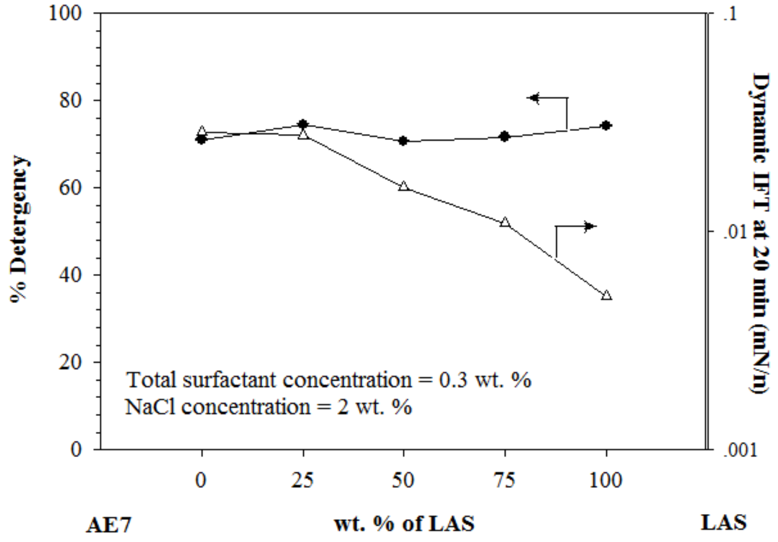


Figure 4.8 Detergency as a function of the selected surfactant concentration at 2 wt. % NaCl and 0.3 wt. % of total surfactant concentration at 30 °C.

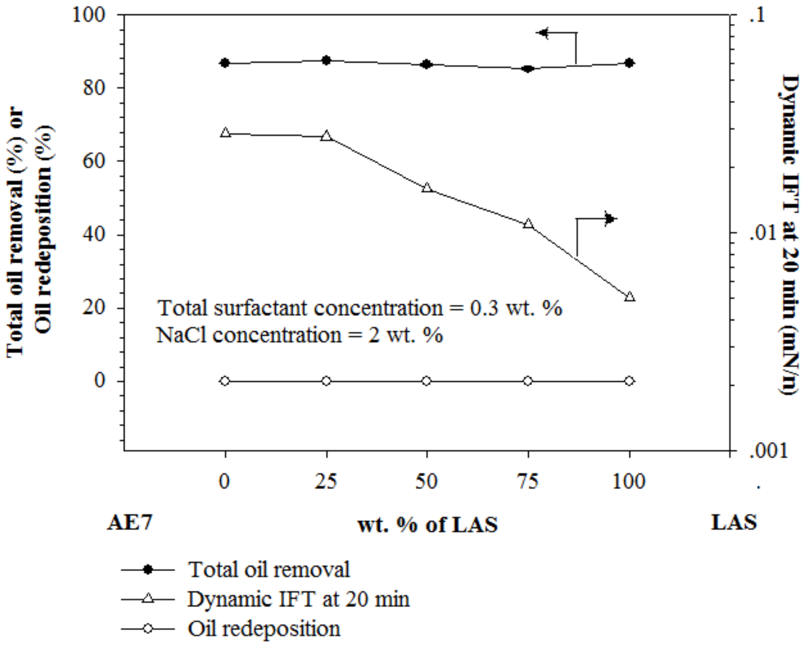


Figure 4.9 Total oil removal as a function of the selected surfactant concentration at 2 wt. % NaCl and 0.3 wt. % of total surfactant concentration at 30 °C.

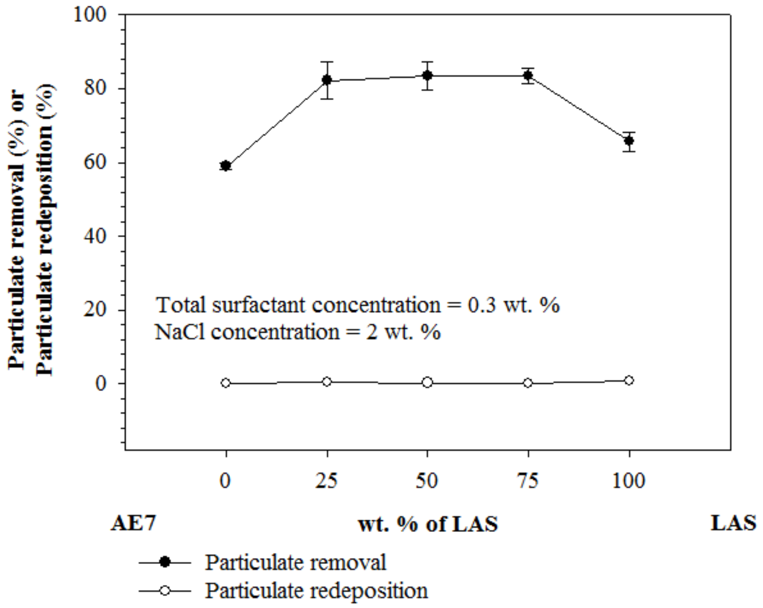


Figure 4.10 Particulate removal as a function of the selected surfactant concentration at 2 wt. % NaCl and 0.3 wt. % of total surfactant concentration at 30 °C.

4.2.4 Comparisons of Detergency, Total Oil Removal and Particulate Soil Removal between the Selected Surfactant Formulation and the Commercial Liquid Detergent

Figure 4.11 shows the detergency of the mixed surfactant systems and the commercial liquid detergent at the same optimum surfactant concentration of 0.3 wt. %. In comparison among the selected surfactant formulations and the commercial liquid detergent, the detergency slightly increases with the highest detergency at 74.5% of 3: 1 of AE7: LAS. It is surprising that the total oil removal with the selected surfactant formulation of 3: 1 of AE7: LAS provides the highest value at 87.6% as shown in Figure 4.12. Hence, the selected surfactant formulation with the weight ratio of 3: 1 of AE7: LAS provides a better performances and higher than the commercial liquid detergent.

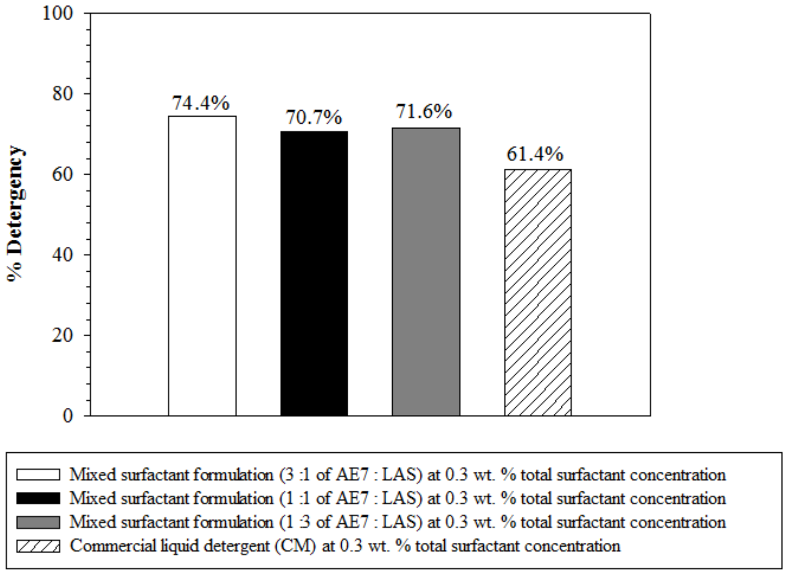


Figure 4.11 Detergency of the selected surfactant formulation and the commercial liquid detergent (CM) at 2 wt. % NaCl and 0.3 wt. % of total surfactant concentration at 30 °C.

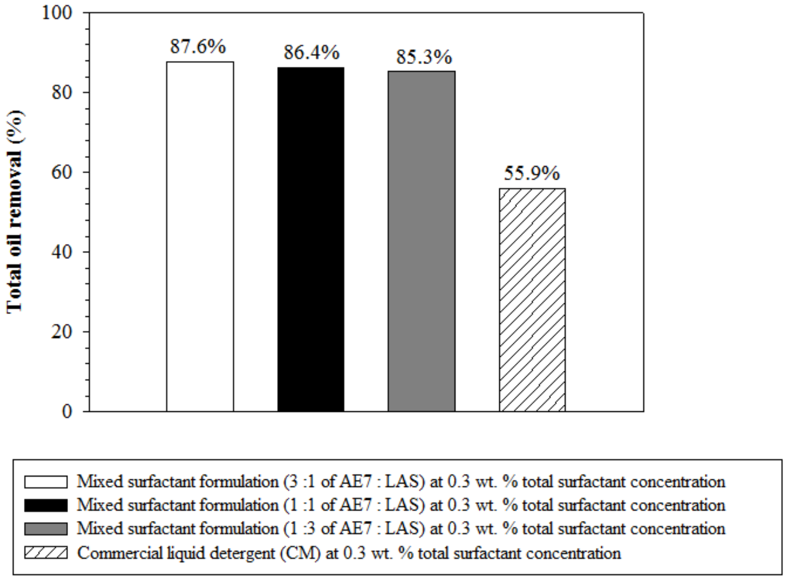


Figure 4.12 Total oil removal of the selected surfactant formulation and the commercial liquid detergent (CM) at 2 wt. % NaCl and 0.3 wt. % of total surfactant concentration at 30 °C.

Figure 4.13 shows the particulate removal of the mixed surfactant systems and the commercial liquid detergent at the same optimum surfactant concentration of 0.3 wt**.** **%**. In comparison among the selected surfactant formulations and the commercial liquid detergent, the particulate removal slightly increases with the highest value at 86.0% of 1: 3 of AE7: LAS. All the selected surfactant formulations. The particulate removal results are much higher than that the commercial liquid detergent since the selected surfactant formulations contain a higher portion of anionic surfactant, leading to good for particulate removal.

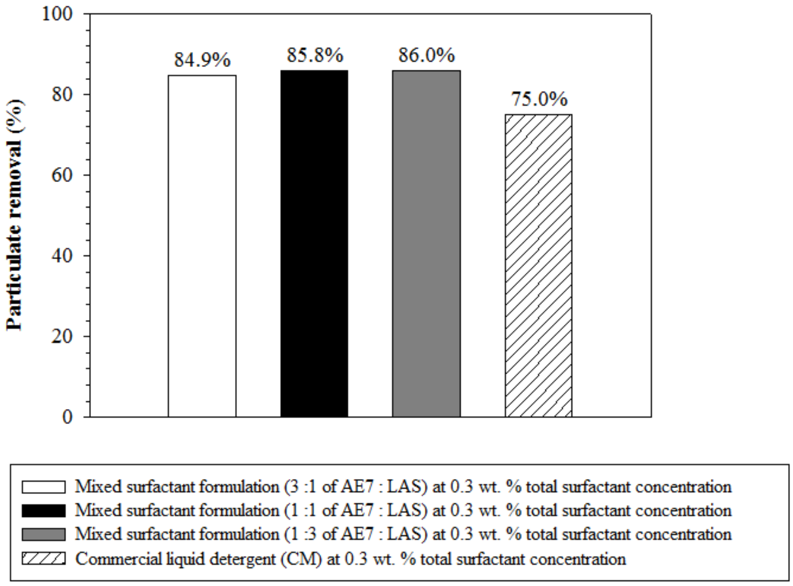


Figure 4.13 Particulate soil removal of the selected surfactant formulation and the commercial liquid detergent (CM) at 2 wt**. %** NaCl and 0.3 wt**. %** of total surfactant concentration at 30 °C.

4.3 Zeta Potentials and Point of Zero Charge Measurement

4.3.1 Point of Zero Charge Results

The point of zero charge (PZC) of kaolinite and polyester/cotton blend fabric are shown in Table 4.1. The PZC of kaolinite and polyester/cotton blend fabric are 1.3 and 2.4, respectively. The results show that all the studied materials are always negatively charged in detergency experiments since The PZC of all studied materials are much lower than the washing pH range (4 to 9).

Table 4.1 Properties of studied materials

Materials	Point of zero charge (PZC)
Kaolinite	1.3
Polyester/cotton blend fabric	2.4

4.3.2 Zeta Potential Measurement

Zeta potential is one of the parameter that can be determining the colloid stability in electrostatically stabilized systems (Marsalek, 2012). The higher of absolute zeta potential, the higher the dispersion stability or the lower of soil re-deposition. The zeta potential of kaolinite and polyester/cotton blend fabric in various surfactant solutions are investigated at 30 °C as shown in Table 4.2. Among the studied surfactant systems, LAS provides the highest zeta potential on both kaolinite and polyester/cotton blend fabric with range of -35.8 to -131.2 mV when DI water is replaced by the 0.3 wt. % surfactant concentration. This changed value in the zeta potential of LAS is much high, which corresponds to the highest electrostatic repulsion force. In addition, the zeta potential of anionic surfactants (MES, LAS, and SDS) increase with increasing surfactant concentration (Chanwattanakit, 2017). For nonionic surfactants (AE7 and AE9), the zeta potential results are insignificant in the values of – 34.7 mV and – 37.6 mV for AE7 and AE9, respectively. Hence, the electrostatic repulsion force of nonionic surfactants have not significant effect. It can be presumed that the water bound to EO groups that will shift the shear plane (Rojvoranun, 2011).

The zeta potential is not only depend on the surfactant systems but also on the salinity concentrations (Gu, 1998). So, Table 4.3 presents the zeta potential of kaolinite and polyester/cotton blend fabric as a function of salinity at 30 °C. As the result, the zeta potential of studied surfactants become less negative at 2 wt. % of NaCl concentration for any fixed surfactant concentration. With increasing electrolyte concentration, the diffuse double layer is compressed with increasing ionic strength, leading to the measured zeta potential decreases (Rios, 2007).

Table 4.4 presents the zeta potential of mixed surfactant between AE7 and LAS in the ratio of 3:1, 1:1, and 1:3, respectively. As expected, the zeta potential become more negative if more LAS is added in the surfactant solution because of the anionic surfactant adsorption, indicating an increasing of electrostatic repulsion forces.

Table 4.2 Zeta potential of kaolinite and polyester/cotton blend fabric in various surfactant solutions at 30 °C

Properties	**ζ of Kaolinite (mV)**	**ζ of Fabric (mV)**	**Summation of ζ (mV)**
DI water	-25.5	-10.3	-35.8
0.3 wt. % AE7	-17.8	-16.9	-34.7
0.3 wt. % AE9	-23.1	-14.5	-37.6
0.3 wt. % MES	-68.4	-20.4	-88.8
0.3 wt. % LAS	-78.1	-53.1	-131.2
0.3 wt. % SDS	-62.4	-35.6	-98.0
0.3 wt. % CM	-73.1	-49.0	-122.1

Table 4.3 Zeta potential of kaolinite and polyester/cotton blend fabric as a function of salinity at 30 °C

Properties	**ζ of Kaolinite (mV)**	**ζ of Fabric (mV)**	**Summation of ζ (mV)**
0.3 wt. % AE7/2 wt. % NaCl	-10.9	-9.9	-20.8
0.3 wt. % AE9/2 wt. % NaCl	-15.5	-9.0	-24.5
0.3 wt. % LAS/2 wt. % NaCl	-34.4	-42.1	-76.5

Table 4.4 Zeta potential of kaolinite and polyester/cotton blend fabric as a function of the selected surfactant concentration at 2 wt**. %** NaCl and 0.3 wt**. %** of total surfactant concentration at 30 °C

Properties	**ζ of Kaolinite (mV)**	**ζ of Fabric (mV)**	**Summation of ζ (mV)**
3:1 of AE7:LAS/2 wt. % NaCl	-16.5	-9.6	-26.1
1:1 of AE7:LAS /2 wt. % NaCl	-21.7	-13.0	-34.7
1:3 of AE7:LAS /2 wt. % NaCl	-30.4	-30.0	-60.4

4.4 Effect of Soiling Procedure on Detergency Performance

The detergency of single and mixed soil in mixed surfactant systems are investigated at 30 °C as shown in Table 4.5. For oily soil removal, detergency, and oil removal did not have a significant effect on soiling procedure with single and mixed soil. However, the particulate soil removal of mixed soil are more effectively removed than single clay. This is probably due to the oil adsorbs on the clay particles and binds them together, resulting in the removal of mixed soil are higher than the results of single soil at 86.0%.

Table 4.5 Detergency performance for different soiling procedure in mixed surfactant systems

Soiling Procedure	**Detergency (%)**	**Total Oil Removal (%)**	**Particulate Soil Removal (%)**
Kaolinite	-	-	62.0
Palm Oil	72.0	87.0	-
Kaolinite/Palm Oil	72.0	86.0	86.0

CHAPTER V
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

In this research, the detergency of mixed oily and particulate soils are investigated with single and mixed surfactant systems. Two soils (oily soil; palm oil and particulate soil; kaolinite), five surfactants; anionic surfactants (MES, LAS and SDS), and nonionic surfactants (AE7 and AE9) and polyester/cotton blend fabric are representatives of soils, surfactants, and fabric. The critical micelle concentration (CMC), dynamic interfacial tension (IFT) and zeta potential of the studied surfactants are related to detergency performance. At any given surfactant concentrations, the detergency efficiency (percentages of detergency, total oil removal and particulate soil removal) increases with increasing surfactant concentration and reaches the maximum at 0.3 wt. % of total surfactant concentration. Among the studied surfactant systems, the anionic surfactant LAS provides the highest total oil removal, corresponding to the lowest the interfacial tension (IFT). Moreover, LAS can provide the highest particulate soil removal due to the highest negatively charges (zeta potential) on both the fabric and soil, resulting in the highest electrostatic repulsion. For the salinity effect, the maximum detergency performance achieves at 2 wt. % NaCl concentration, which corresponds to the minimum IFT. The results imply that the reduction of repulsive force between head group of the surfactant molecules by the Na+ counter ion effect, leading to enhance the surfactant adsorption, resulting in detergency improvement. In addition, the mixed surfactant system of LAS and AE7 exhibit the improvement of detergency performance as compared with the commercial liquid detergent. Interestingly, the particulate soil removal of the selected surfactant formulation on any mixing ratio is found to be significantly higher than that of the single surfactant systems and the commercial liquid detergent since the synergistic effect between the head group of mixed surfactant systems (AE7 and LAS) can balance the electrostatic repulsion, leading to higher particulate soil removal. From the different soiling procedure, the binding properties of oil and clay are observed to be an important factor to detergency performance in the mixed surfactant systems, thus better the particulate soil removal.

5.2 Recommendations

In this research, the detergency conditions in single and mixed surfactant systems were studied at a constant temperature of 30 °C with the presence of salinity. For further study, other important factors affected to the detergency performance such as pH, temperature, fabric type, water hardness should be investigated. Furthermore, the adsorption isotherm of single and mixed surfactant on fabric and particulate soil should be investigated which can help to better understanding of particulate soil removal.

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APPENDICES

Appendix A Experimental Data of CMC Measurement

Table A1 Surface Tension of AE7

Surfactant concentration (µM)	IFT (mN/m)
1	55.7
5	50.0
10	47.5
25	43.4
50	34.0
75	34.3
100	34.0
500	34.0
1000	34.0

Table A2 Surface Tension of AE9

Surfactant concentration (µM)	IFT (mN/m)
1	54.3
5	47.9
10	46.5
25	39.2
50	35.2
75	33.3
100	33.4
500	33.4
1000	33.4

Table A3 Surface Tension of MES

Surfactant concentration (µM)	IFT (mN/m)
200	57.0
300	56.0
400	53.0
500	51.0
600	48.5
700	46.5
800	44.0
900	42.0
1000	40.0
2000	36.8
3000	36.2
5000	36.3

Table A4 Surface Tension of LAS

Surfactant concentration (µM)	IFT (mN/m)
100	59.0
300	47.6
500	48.2
800	44.4
1000	41.6
3000	37.7
5000	37.1
8000	37.1
10000	36.9

Table A5 Surface Tension of SDS

Surfactant concentration (µM)	**IFT (mN/m)**
500	59.0
600	55.0
700	54.0
800	53.0
900	52.0
1000	51.0
2000	48.0
3000	45.0
4000	41.0
5000	40.0
6000	36.5
7000	35.5
8000	35.5
9000	35.3

Appendix B Experimental Data of Zeta Potential Measurement

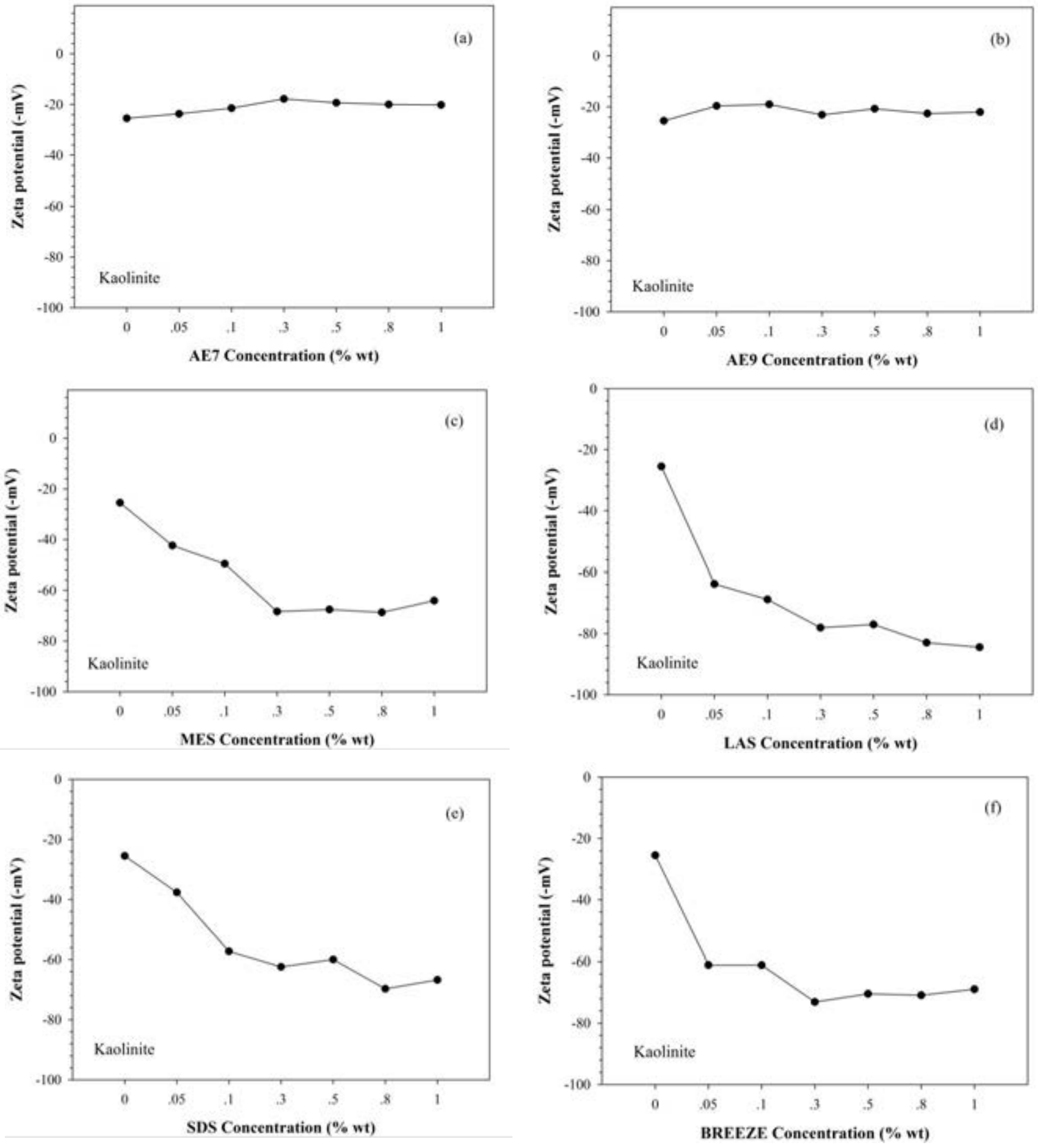

Figure B1 Zeta potential of (a) AE7, (b) AE9, (c) MES, (d) LAS, (e) SDS, and (f) the commercial liquid detergent (Breeze) on kaolinite at 30 °C.

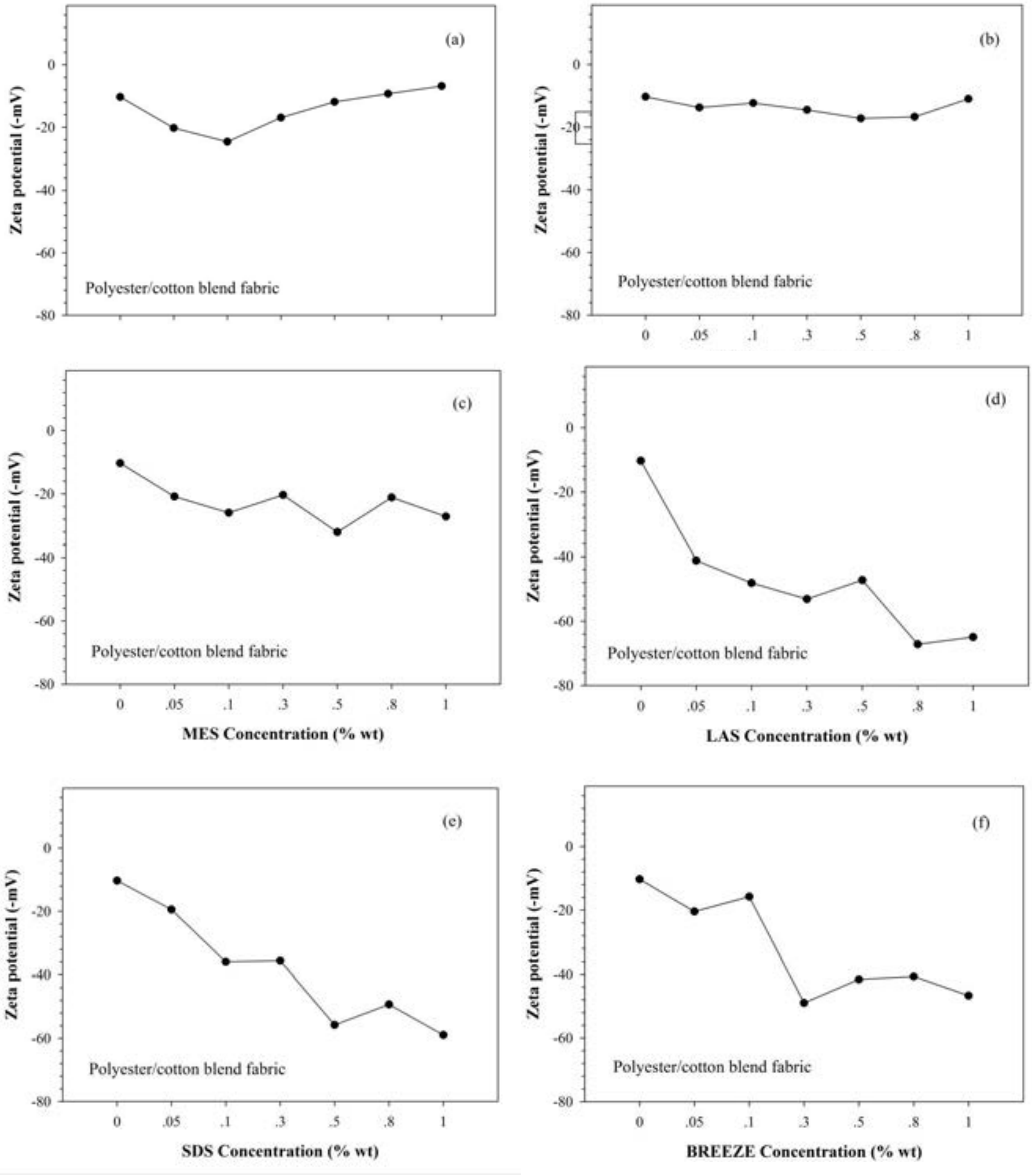

Figure B2 Zeta potential of (a) AE7, (b) AE9, (c) MES, (d) LAS, (e) SDS, and (f) the commercial liquid detergent (Breeze) on polyester/cotton blend fabric at 30 °C.

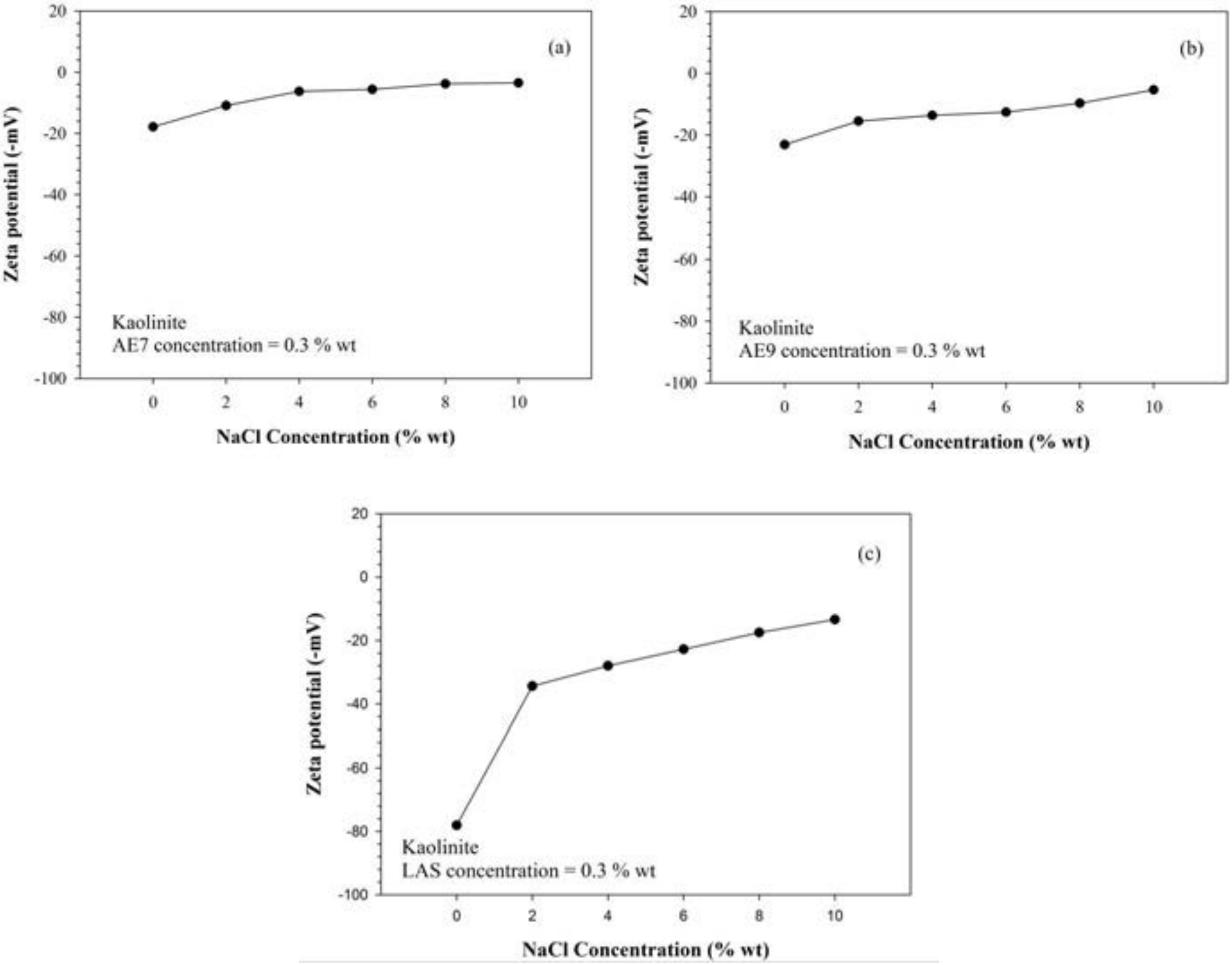

Figure B3 Zeta potential of (a) AE7, (b) AE9, and (c) LAS on kaolinite as a function of salinity.

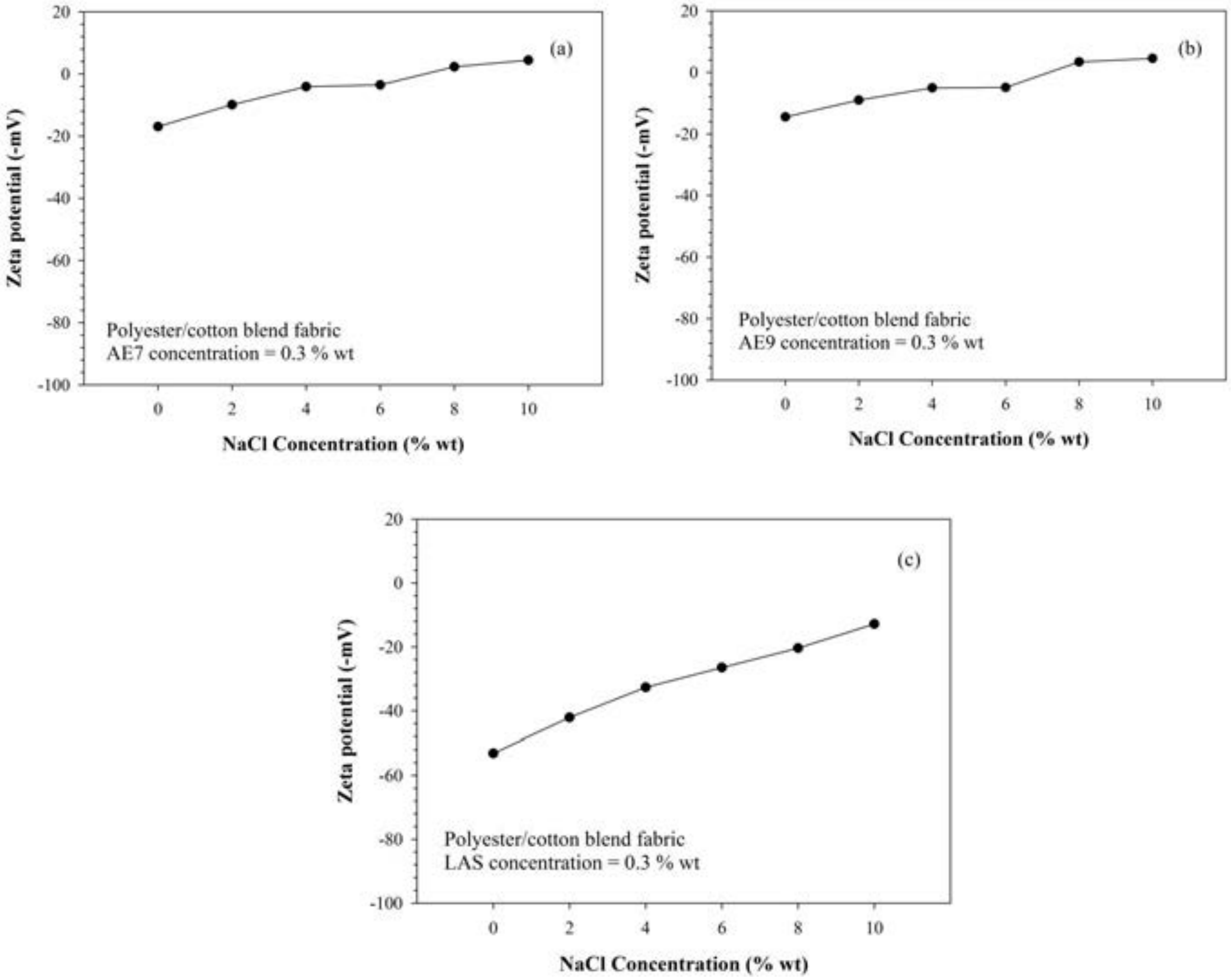

Figure B4 Zeta potential of (a) AE7, (b) AE9, and (c) LAS on polyester/cotton blend fabric as a function of salinity.

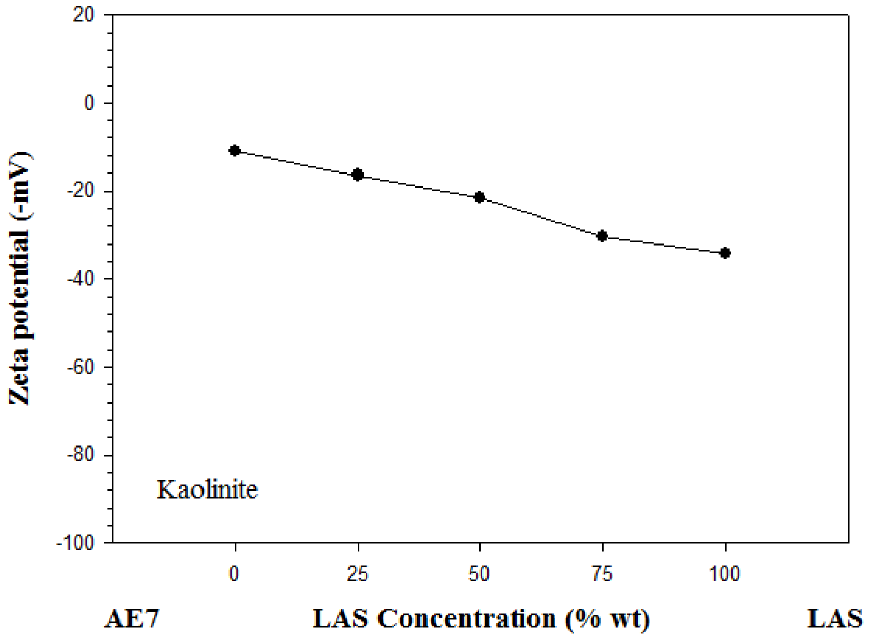

Figure B5 Zeta potential on kaolinite as a function of the selected surfactant concentration at 2% NaCl and 0.3% of total surfactant concentration with a constant temperature of 30 °C.

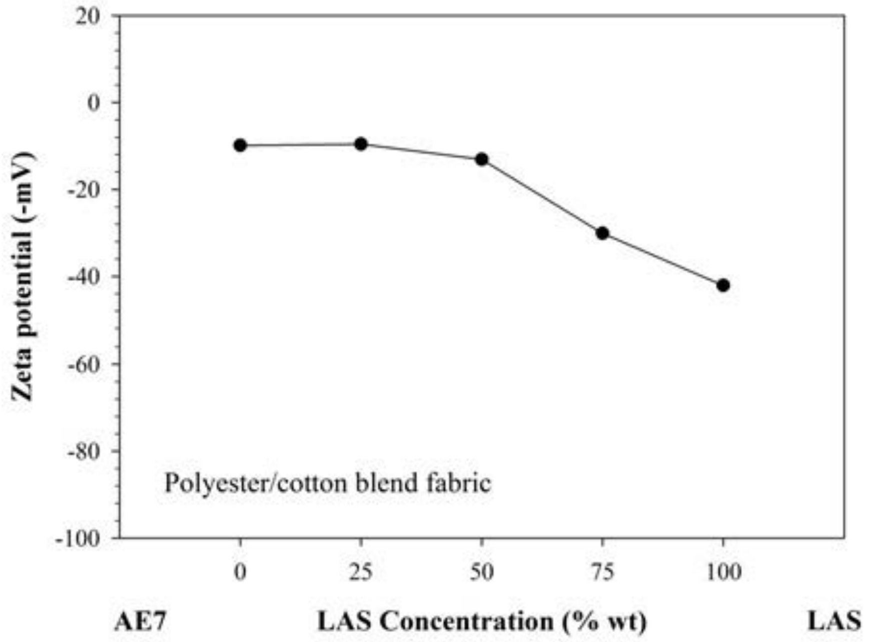

Figure B6 Zeta potential on polyester/cotton blend fabric as a function of the selected surfactant concentration at 2% NaCl and 0.3% of total surfactant concentration with a constant temperature of 30 °C.

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