

MICROEMULSION FORMATION AND DETERGENCY WITH OILY SOIL



Parichat Tanthakit

A Dissertation Submitted in Partial Fulfilment of the Requirements
for the Degree of Doctor of Philosophy
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
and Case Western Reserve University

2009

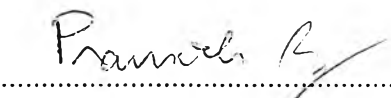
522101

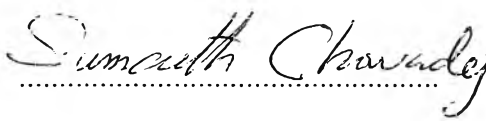
Thesis Title: Microemulsion Formation and Detergency with Oily Soil
By: Parichat Tanthakit
Program: Petrochemical Technology
Thesis Advisors: Assoc. Prof. Sumaeth Chavadej
Dr. Chantra Tongcumpou
Prof. John F. Scamehorn

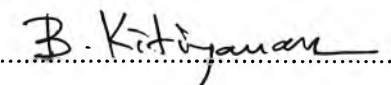
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

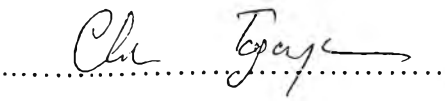

..... Dean
(Asst. Prof. Pomthong Malakul)

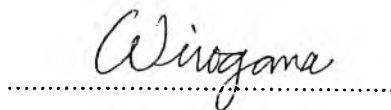
Thesis Committee:

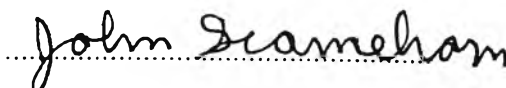

.....
(Assoc. Prof. Pramoch Rangsunvigit)


.....
(Assoc. Prof. Sumaeth Chavadej)


.....
(Asst. Prof. Boonyarach Kitiyanan)


.....
(Dr. Chantra Tongcumpou)


.....
(Asst. Prof. Wirogana Ruengphrathuengsuka)


.....
(Prof. John F. Scamehorn)

ABSTRACT

4791006063: Petrochemical Technology

Parichat Tanthakit: Microemulsion Formation and Detergency with Oily Soil

Thesis Advisors: Assoc. Prof. Sumaeth Chavadej, Dr. Chantra Tongcumpou and Prof. John F. Scamehorn 126 pp.

Keywords: Detergency/ Microemulsion/ Motor Oil/ Mixed Surfactant

The ultimate objective of this work was to form microemulsions with different oils at low salinity for the detergency process. In this study, three surfactants—alkyl diphenyl oxide disulfonate (ADPODS, Dowfax 8390), bis (2-ethylhexyl) sulfosuccinic acid sodium salt (AOT), and sorbitan monooleate (Span 80)—were used to obtain a proper balance between hydrophobicity and hydrophilicity in order to form microemulsions with motor oil at low salinity. Under a microemulsion-based formulation, the motor oil removal increased with increasing total surfactant concentration and the maximum oily soil removal was around 0.1% total surfactant concentration for all three types of fabrics—pure cotton, polyester/cotton (65/35), blend and pure polyester). Detergency was found to improve with increasing hydrophilicity of the fabric with cotton being the cleanest after washing and polyester the most difficult to clean. An interesting characteristic of microemulsion-based formulations is that a substantial fraction of oil removal was found to occur in the rinse step. In this work, the low oil removal in the wash step was found to result from the ultralow oil/water interfacial tension and the surfactant loss due to the surfactant adsorption onto the fabric surface. From the results, the number of rinses and the volume of water per rinse can profoundly affect detergency in these systems, and it was found that the higher the amount of rinse water, the lower the residual surfactant on the fabric surface.

In this study, the effects of water hardness and builder on both the phase diagrams of aqueous microemulsions with motor oil and the laundry detergency of oil removal from a polyester/cotton blend was investigated. Water

hardness and builder were found to insignificantly affect the microemulsion phase diagram with motor oil. A mixed surfactant system of 0.1% $C_{14-15}(PO)_3SO_4Na$ (Alfotera) and 5% $C_{12-14}H_{25-29}O(EO)_5H$ (Tergitol) at 4% salinity was used to study the effects of water hardness; the addition of any studied builder—sodium tripolyphosphate (STPP) or ethylenediaminetetraacetic acid (EDTA) – showed approximately the same effect on oil removal. From the detergency results, the total oil removal decreased with increasing water hardness while the interfacial tension (IFT) increased. When hard water was used in laundering, the total oil removal was improved at a certain level, even though an excess amount of STPP or EDTA was added in the selected formulation.

บทคัดย่อ

ปาริฉัตร ตัณฑกกิจ: การเกิดไมโครอิมัลชันเพื่อประยุกต์ใช้ในกระบวนการซักล้างน้ำมัน (Microemulsion Formation and Detergency with Oily Soil) อ. ที่ปริกษา: รศ.ดร. สุเมธ ชวเดช ดร. จันทรา ทองคำเกา และ ศ.ดร. จอห์น เอฟ สกามีฮอร์น 126 หน้า

วัตถุประสงค์หลักของงานวิจัยนี้ คือ การสร้างระบบไมโครอิมัลชันกับน้ำมันชนิดต่างๆ ในปริมาณเกลือต่ำเพื่อใช้กับกระบวนการทำความสะอาด โดยในการศึกษานี้ สารลดแรงตึงผิว 3 ชนิดถูกเลือกมาใช้ในการเกิดไมโครอิมัลชันกับน้ำมันเครื่อง ได้แก่ คาวแฟล็กซ์ 8390, เอโอที และ ซอร์บิแทนโมโนโอลิเอต หรือ สเปน 80 ซึ่งสามารถสร้างความสมดุลที่เหมาะสมของค่าความสมดุลของความชอบน้ำและความชอบน้ำมันในการทำให้เกิดไมโครอิมัลชันกับน้ำมันเครื่อง สำหรับสูตรที่ใช้ไมโครอิมัลชันเป็นพื้นฐาน พบว่าประสิทธิภาพของการทำความสะอาดน้ำมันเครื่องเพิ่มขึ้นเมื่อปริมาณความเข้มข้นของสารลดแรงตึงผิวเพิ่มขึ้น และพบว่าที่ปริมาณ 0.1 เปอร์เซ็นต์ของความเข้มข้นสารลดแรงตึงผิวให้ประสิทธิภาพสูงสุดในการทำความสะอาดบนวัสดุ 3 ชนิด คือ ผ้าฝ้าย, ผ้าโพลีเอสเตอร์ และ ผ้าผสมโพลีเอสเตอร์/ฝ้าย นอกจากนี้ยังพบว่า การทำความสะอาดน้ำมันเครื่องบนผ้าฝ้ายให้ประสิทธิภาพสูงสุด และการทำความสะอาดบนผ้าโพลีเอสเตอร์ให้ประสิทธิภาพต่ำที่สุดคุณลักษณะที่น่าสนใจของประสิทธิภาพการซักล้างโดยใช้สูตรการทำความสะอาดที่อาศัยไมโครอิมัลชันเป็นพื้นฐาน คือ ปริมาณของน้ำมันเครื่องโดยมากจะถูกชะล้างออกในขั้นตอนการล้าง ซึ่งพบว่ามีปริมาณน้ำมันเครื่องส่วนน้อยที่ถูกทำความสะอาดในขั้นตอนการซัก ซึ่งมีผลมาจากค่าแรงตึงผิวระหว่างวัฏภาคที่ต่ำและการสูญเสียสารลดแรงตึงผิวซึ่งมาจากการดูดซับของสารลดแรงตึงผิวบนผิวผ้า ในขั้นตอนการซัก ทั้งนี้จากผลการศึกษา ยังพบว่า ปริมาณน้ำและจำนวนครั้งการซักล้างทำความสะอาดมีผลต่อประสิทธิภาพในการทำความสะอาด และพบว่า ปริมาณสารลดแรงตึงที่ตกค้างอยู่บนผิวผ้าหลังกระบวนการทำความสะอาดลดลงเมื่อปริมาณน้ำในการล้างเพิ่มขึ้น

ในการศึกษานี้ ยังได้ทำการศึกษาผลกระทบของน้ำกระด้างและสารเติม (builder) ต่อการเกิด ไมโครอิมัลชันและประสิทธิภาพการทำความสะอาด ซึ่งพบว่า น้ำกระด้างและสารเติม มีผลน้อยต่อการเกิดไมโครอิมัลชัน โดยในการศึกษานี้ ได้เลือกระบบสารลดแรงตึงผิวผสมระหว่าง 0.1 เปอร์เซ็นต์ของอัลโฟเทอรา และ 5 เปอร์เซ็นต์ของเทอจิดอล และ 4 เปอร์เซ็นต์ของเกลือโซเดียมคลอไรด์ ใช้ในการทดสอบเปรียบเทียบการทำความสะอาดในระบบที่มีสารเติมต่างกัน 2

ชนิด ซึ่งพบว่า ให้ผลการทำความสะอาดไม่แตกต่างกันมากนัก และจากการศึกษา พบว่า เมื่อน้ำ กระจกมีความเข้มข้นสูงขึ้น ประสิทธิภาพการซักล้างจะต่ำลง ในขณะที่ค่าแรงตึงผิวเพิ่มขึ้น นอกจากนี้ ยังพบว่า เมื่อใช้สารเคมีในระบบการทำความสะอาดในน้ำกระจก จะมีผลทำให้ ประสิทธิภาพการซักล้างเพิ่มขึ้นถึงปริมาณหนึ่งเท่านั้น ถึงแม้ว่า จะใส่สารเคมีลงไปในปริมาณที่ มากเกินพอก็ตาม

ACKNOWLEDGEMENTS

This work has brought me a lot of knowledge in the area of detergency. It would not have been possible without the assistance from many persons and organizations. The author would like to acknowledge all of them for their support towards this work.

First of all, the author gratefully acknowledge Assoc. Prof. Sumaeth Chavadej as a Thai thesis advisor and Dr. Chantra Tongcumpou as a coadvisor, for several constructive suggestions and discussion throughout the course of this work. The author would like to express my gratefulness to, Prof. John F. Scamehorn, an oversea advisor for his guidance, suggestion and encouragement throughout this work.

The Royal Golden Jubilee PhD. Program (RGJ) under the Thailand Research Fund is greatly acknowledged for providing a Ph.D. scholarship to the author. Mr. Robert J. Wright is acknowledged for his valuable advice toward papers and thesis correction.

The author is indebted to Ms. Anuradee Withayapanyanon, Dr. Ummarawadee Yanatatsaneejit and all friends in the surfactant group at University of Oklahoma for their valuable suggestions and encouragements.

The author would like to express her sincere gratitude to all faculties and staff at the PPC all assistance to facilitate her thesis work.

Lastly, the author would like to offer sincere gratitude to her family especially, her beloved aunt for their love, caring, sharing her problems, supporting and understanding her all the time.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	v
Acknowledgements	vii
Table of Contents	viii
List of Figures	xiv
List of Tables	xxii
CHAPTER	
I INTRODUCTION	1
II BACKGROUND AND LITERATURE REVIEW	4
2.1 Microemulsions	4
2.1.1 Types of Microemulsios	4
2.2 Application of Microemulsion for Detergency	7
2.3 Principal Mechanisms of Oily Soil Removal	8
2.3.1 Roll-up Mechanism	9
2.3.2 Emulsification	10
2.3.3 Solubilization	11
2.4 Maximum Detergency (D_{\max}) and Spreading Effect	12
2.5 Factors Affecting Oily Soil Removal	13
2.5.1 Nature of Oil	13
2.5.2 Surfactant System	14
2.5.3 Salt	15
2.5.4 Substrate	15
2.5.5 Water Hardness	16
2.5.6 Builders	16

CHAPTER	PAGE
4.3.3 Surface Tension Measurements	28
4.3.4 Fish Diagram Study	29
4.3.5 Fabric Pretreatment and Soiling Procedure	29
4.3.6 Laundry Procedure	30
4.3.7 Oil Removal Measurements	30
4.3.8 Dynamic IFT Measurements	30
4.4 Results and Discussion	31
4.4.1 Effect of Surfactant Composition on Microemulsion Formation	31
4.4.2 Effect of Oil-to-Surfactant solution Ratio	33
4.4.3 Effect of Surfactant Concentration on Detergency Performance	34
4.4.4 Effect of Salinity on Detergency Performance	36
4.4.5 Fish Diagram of Motor Oil with the Selected Formulation	37
4.4.6 Correlation of Microemulsion Formation and Detergency Performance	41
4.4.7 Effects of Quantity of Rinsing Water and Number of Rinses on Oil Removal	43
4.4.8 Correlation of Detergency Performance and Equilibrium IFT in the Rinse Step	48
4.5 Acknowledgements	49
4.6 References	50
V MICROEMULSION FORMATION AND DETERGENCY OF OILY SOIL: V RESIDUAL SURFACTANT ON FABRIC	55
5.1 Abstract	55

CHAPTER	PAGE
5.2 Introduction	56
5.3 Experimental Procedures	58
5.3.1 Materials	58
5.3.2 Phase Studies	59
5.3.3 Surface Tension Measurement	59
5.3.4 Fish Diagram Study	59
5.3.5 Fabric Preparation and Soiling Method	60
5.3.6 Laundry Procedure	60
5.3.7 Oil Removal Measurement	61
5.3.8 Dynamic IFT Measurement	61
5.3.9 Surfactant Concentration Measurement	61
5.4 Results and Discussion	61
5.4.1 Effect of Surfactant Composition on Microemulsion Formation	61
5.4.2 Effect of Surfactant System on Detergency Performance	64
5.4.3 Fish Diagram of Motor Oil with the Selected Formulation	66
5.4.4 Effect of Amount of Rinsing Water on Oil Removal	71
5.4.5 Correlation between IFT and the Total Oil Removal Using the Selected Formulation	72
5.4.6 Correlation between IFT of Washing Solution and Oil Removal in the Wash Step	73
5.4.7 Correlation between Equilibrium IFT and Oil Removal in Washing Process	74
5.4.8 Correlation between Remaining ADPODS in Washing Solution and Detergency Efficiency	75

CHAPTER	PAGE
5.5 Acknowledgements	83
5.6 References	84
VI MICROEMULSION FORMATION AND DETERGENCY OF OILY SOIL: EFFECT OF WATER HARDNESS AND BUILDER	88
6.1 Abstract	88
6.2 Introduction	89
6.3 Experimental Procedures	90
6.3.1 Materials	90
6.3.2 Phase Studies	91
6.3.3 Surface Tension Measurement	92
6.3.4 Dynamic IFT Measurement	92
6.3.5 Fabric Preparation and Soiling Method	92
6.3.6 Laundry Procedure	93
6.3.7 Oil Removal Measurement	93
6.3.8 Analysis of Water Hardness	93
6.4 Results and Discussion	94
6.4.1 Effect of Surfactant Composition on the Microemulsion Phase Diagram	94
6.4.2 Effect of Water Hardness on Microemulsion Formation and IFT	98
6.4.3 Effect of Total Surfactant Concentration on Detergency Performance	103
6.4.4 Effect of Water Hardness and Builder on Detergency Performance	106

CHAPTER	PAGE
6.4.5 Effect of Builder on Free Divalent Cation Concentration	110
6.5 Acknowledgements	112
6.6 References	112
VII CONCLUSIONS AND RECOMMENDATIONS	117
7.1 Conclusions	117
7.2 Recommendations	118
REFERENCES	119
CURRICULUM VITAE	124

LIST OF FIGURES

FIGURE	PAGE
CHAPTER II	
2.1	The relationship between microemulsion structure and interfacial tension of salinity scan and HLB value 6
2.2	The contact angle between an oil droplet and substrate in bath 10
2.3	Roll-up mechanism shows complete removal of oil droplets from substrate by hydraulic currents when $\theta > 90^\circ$ 10
2.4	Snap-off mechanism shows incomplete removal of oil droplets from substrate by hydraulic currents when $\theta < 90^\circ$. A small droplet remains attached to the substrate 10
CHAPTER III	
3.1	Experimental procedure of microemulsion formation 21
CHAPTER IV	
4.1	Solubilization parameters (SP) and Winsor Types of microemulsions as a function of salinity at an initial oil to water volumetric ratio of 1 to 1; (a) 2% ADPODS and 2% Span 80 were fixed, (a-1) 3% AOT, (a-2) 4% AOT and (a-3) 5% AOT; (b) 2% ADPODS and 5% AOT were fixed, (b-1) 2% Span 80, (b-2) 4% Span 80 and (b-3) 5% Span 80; (c) 5% AOT and 5% Span 80 were fixed, (c-1) 1.5% ADPODS, (c-2) 2% ADPODS and (c-3) 3% ADPODS. SP* is SP at optimum salinity S* where SP of oil (SPo) equals SP of water (SPw) into middle phase microemulsion phase. 32

FIGURE		PAGE
4.2	Equilibrium IFT at different salinities and oil to surfactant solution volumetric ratios with the selected formulation (1.5% ADPODS, 5% AOT and 5% Span 80) at 30 °C.	34
4.3	Effect of total surfactant concentration on oil removal at the optimum salinity (2.83%) with the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80).	35
4.4	Effects of NaCl concentration on oil removal at different salinities with 0.115% total surfactant concentration of the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80) and two rinse steps.	36
4.5	Schematic representation of normal fish phase diagram. Roman numerals refer to the Winsor Type microemulsion existing at that condition.	38
4.6	Equilibrium IFT and dynamic IFT at 20 min as a function of total surfactant concentration at 30 °C using the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80 with 2.83% NaCl).	38
4.7	Surface tension of the mixed surfactant system with and without salinity for the motor oil system	39
4.8	Fish phase diagram of our formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80) at an oil-to-water volumetric ratio of 1 to 1 at 30 °C.	41
4.9	Oil removal and equilibrium IFT between washing solution and oil as a function of salinity with the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80) and two rinses of 1000 mL each.	42

FIGURE	PAGE
4.10 Oil removal in each cleaning step with different volumes of rinsing water and different times of rinses using the selected formulation (W = the wash step ; R1= the first rinse ; R2 = the second rinse ; R3 = the third rinse and so on)	44
4.11 Cumulative oil removal with different volumes of rinsing water and different numbers of rinse step using the selected formulation of total surfactant concentration of 0.115% (W = the wash step ; R1= the first rinse; R2 = the second rinse ; R3 = the third rinse and so on)	44
4.12 Dynamic IFT between rinsing water and dyed oil with the selected formulation and total surfactant concentration of 0.115%: (a) 2 rinses with 1000 mL each (b) 4 rinses with 500 mL each and (c) 6 rinses with 333.33 mL each	46
4.13 Schematic representation of normal fish phase diagram. Roman numerals refer to the Winsor Type microemulsion existing at that condition.	47
4.14 Oil removal in each step related to the equilibrium IFT between washing (or rinsing) solution and oil with the selected formulation (13 parts ADPODS, 43.5 parts AOT, and 43.5 parts Span 80).	49

CHAPTER V

5.1 Solubilization parameters (SP) and Winsor Types of microemulsions as a function of salinity at an initial oil-to-water volumetric ratio of 1 to 1; (a) 1% ADPODS and 3% Span 80 were fixed, (a-1) 3% AOT, (a-2) 4% AOT and (a-3) 5% AOT; (b) 5% AOT and 3% Span 80 were fixed, (b-1) 0.5% ADPODS, (b-2) 0.75% ADPODS and (b-3) 1%	63
---	----

FIGURE	PAGE
ADPODS; (c) 0.5% ADPODS and 5% AOT were fixed, (c-1) 1% Span 80, (c-2) 2% Span 80 and (c-3) 3% Span80. SP* is SP at optimum salinity (S*).	
5.2 Effect of surfactant system (both single and mixed surfactant systems) on both total oil removal and IFT on a polyester/cotton blend (65/35) at various salinities and a total surfactant concentration of 0.119% compared to a commercial liquid detergent.	65
5.3 Equilibrium and dynamic IFT at 20 min as a function of total surfactant concentration at 30 °C using the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio).	67
5.4 Surface tension plot with total surfactant concentration of the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio) with and without salinity.	68
5.5 Fish phase diagram of the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio) at an oil-to-water volumetric ratio of 1 to 1 at 30 °C.	69
5.6 The cumulative oil removal of different rinsing methods (a) 1000 mL, (b) 500 mL, and (c) 333.33 mL for each rinse using the selected formulation of total surfactant concentration of 0.119% at different salinities.	70
5.7 Total oil removal with different volumes of rinsing water and different salinities using the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio).	71
5.8 Total oil removal and IFT of the washing solution as a function of salinity with the 0.119% surfactant concentration of the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio) and two rinses of 1000 mL each.	72

FIGURE		PAGE
5.9	The relationship between the IFT and the remaining ADPODS in washing solution and the oil removal in the wash step as a function of salinity with the 0.119% surfactant concentration of the selected formulation (1:10:6 of ADPODS:AOT:Span 80 ratio).	74
5.10	Oil removal in each step related to the equilibrium IFT between washing solution and oil at different salinities with the selected formulation (1:10:6 of ADPODS:AOT:Span 80).	75
5.11	The ADPODS remaining in the rinsing water after the first or second rinse steps at various salinities and different amounts of rinsing water.	77
5.12	The amount of ADPODS left in different rinse steps and the total oil removal after (a) the first rinse (b) the second rinse at different amounts of rinsing water.	78
5.13	The percentage of residual ADPODS on the fabric surface at different rinse methods based on the initial ADPODS and 100 g fabric (a) after first rinse and (b) after second rinse.	80
5.14	The residual ADPODS on fabric in each step based on the initial ADPODS amount (a) on the soiled fabric (b) on unsoiled fabric at different rinsing methods under the selected formulation (1:10:6 of ADPODS:AOT:Span 80) with the optimum salinity and at 30 °C.	82

FIGURE	PAGE
CHAPTER VI	
6.1 Solubilization parameters (SP) and phase height fraction as a function of NaCl concentration and $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$ concentration at an initial oil-to-water volumetric ratio of 1 to 1 and 5% $C_{12-14}\text{H}_{25-29}\text{O}(\text{EO})_5\text{H}$ and: (a-1) 0.1% $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$, (a-2) 0.3% $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$, (a-3) 0.5% $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$, and (a-4) 1% $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$.	95
6.2 Solubilization parameters (SP) and phase height fraction as a function of NaCl concentration and $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$ concentration at an initial oil-to-water volumetric ratio of 1 to 1 and 0.1% $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$ and: (b-1) 3% $C_{12-14}\text{H}_{25-29}\text{O}(\text{EO})_5\text{H}$, (b-2) 5% $C_{12-14}\text{H}_{25-29}\text{O}(\text{EO})_5\text{H}$, and (b-3) 8% $C_{12-14}\text{H}_{25-29}\text{O}(\text{EO})_5\text{H}$.	97
6.3 Solubilization parameters (SP) as a function of NaCl concentration and water hardness at an initial oil-to-water volumetric ratio of 1 to 1 with 5% $C_{12-14}\text{H}_{25-29}\text{O}(\text{EO})_5\text{H}$ and 0.1% $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$.	98
6.4 Equilibrium IFT between the dyed motor oil and the aqueous solution of the selected formulation (2 parts $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$ and 98 parts $C_{12-14}\text{H}_{25-29}\text{O}(\text{EO})_5\text{H}$) at different NaCl concentrations and water hardness levels.	99
6.5 Equilibrium and dynamic IFT at 20 min as a function of total surfactant concentration at 30 °C using the selected formulation (0.1% $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$ and 5% $C_{12-14}\text{H}_{25-29}\text{O}(\text{EO})_5\text{H}$, or 2 parts $C_{14-15}(\text{PO})_3\text{SO}_4\text{Na}$ and 98 parts $C_{12-14}\text{H}_{25-29}\text{O}(\text{EO})_5\text{H}$) with 4% salinity.	101
6.6 Surface tension of the mixed surfactant system with 4% salinity for the motor oil system.	101

FIGURE	PAGE
6.7 Fish phase diagram of the selected formulation (2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$) at an oil-to-water volumetric ratio of 1 to 1 at different degrees of water hardness.	102
6.8 Effect of total surfactant concentration on oil removal of the selected formulation (2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$) at 4% of salinity and 30 °C.	104
6.9 Standard photographs of: (a) unsoiled fabric, (b) soiled fabric with dyed motor oil, and (c) fabric after washing with 0.3% total surfactant concentration of the selected formulation (2 parts $C_{14-15}(PO)_3SO_4Na$ and 98 parts $C_{12-14}H_{25-29}O(EO)_5H$) with the 4% salinity.	104
6.10 The total oil removal and the equilibrium IFT between oil and washing solution of the selected formulation at 4% salinity with different degrees of water hardness using a polyester/cotton blend at 30 °C.	106
6.11 The total oil removal and the equilibrium IFT between oil and washing solution of the selected formulation at 4% salinity with different degrees of water hardness using a polyester/cotton blend at 30 °C.	107
6.12 Total oil removal at different builder concentrations using 0.3% total surfactant concentration of the selected formulation without adding water hardness at 30 °C.	109
6.13 Total oil removal at different builder-to-water hardness molar ratios using a 0.3% total surfactant concentration, prepared from the selected formulation and 500 ppm water hardness in both washing solution and rinsing water.	109

FIGURE		PAGE
6.14	Amount of free divalent cations remaining in solution at different builder-to-water hardness molar ratios with and without the polyester/cotton blend fabric, in the absence of surfactants.	110
6.15	Amount of free divalent cations remaining in solution at different builder-to-water hardness molar ratios with and without the polyester/cotton blend fabric using a washing solution containing 0.3% total surfactant concentration prepared from the selected formulation.	111

LIST OF TABLES

TABLE		PAGE
CHAPTER VI		
6.1	The detergency performance of motor oil removal compared to previous studies	105