MICROEMULSION FORMULATION FOR LOW TEMPERATURE CLEANING USING NOVEL SURFACTANT SYSTEMS

Parichat Phaodee

A Thesis Submitted in Partial Fulfillment 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

2015

Thesis Title: Microemulsion Formulation for Low Temperature Cleaning

using Novel Surfactant Systems

By: Parichat Phaodee

Program: Petrochemical Technology

Thesis Advisors: Dr. Ampira Charoensaeng

Prof. David A. Sabatini

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

.... College Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

(Dr. Ampira Charoensaeng)

(Prof. David A. Sabatini)

(Asst. Prof. Boonyarach Kitiyanan)

(Dr. Chodchanok Attaphong)

ABSTRACT

5671023063: Petrochemical Technology Program

Parichat Phaodee: Microemulsion Formulation for Low Temperature Cleaning using

Novel Surfactant Systems.

Thesis Advisors: Dr. Ampira Chareonsaeng, and

Prof. David A. Sabatini 72 pp.

Keywords: Microemulsions/ Novel surfactants/ Palm olein/ Semi-solid fat/

Solubilization

The eco-friendly surfactant detergency in future is motivated by environmental saving. The design of cold water detergency to perform well requires formulation of detergency not only making them effective but also highly solubilizing semi/solid fats in vegetable oil at low temperature. One of the most important mechanisms of cleaning is solubilization capacity of surfactant system. Therefore, this work intended toform vegetable oil based microemulsions for cleaning applications. The surfactant and oil interactions was investigated through the microemulsion phase scan, IFT measurement and solubilization capacity. The anionic $[C_{14-15}H_{29-31}-(PO)_8-SO_4Na]$ and nonionic $C_{12-14}H_{27-29}-(EO)_n-OH$ with three differences in EO groups (n=3, 5, and 9) and their mixture were investigated. Palm olein and palm strearin were selected and represented as a liquid and a solid vegetable oil, respectively. The results indicated that middle phase microemulsion with palm olein was difficult to observe for all surfactant systems. The IFT results showed that at 4.6%w/v NaCl of single and mixed surfactant systems provided the lowest IFT value for each surfactant system. The result of solubilization capacity with palm stearin showed the highest solubilization capacity by mixed surfactant system $[C_{14-15}H_{29-31}-(PO)_8-SO_4Na/C_{12-14}H_{27-29}-(EO)_3-OH, 1:1 by molar ratio]$ at 4.6%w/v NaCl, representing by the molar solubilization ratio (MSR) value of 0.399 and micelle partition coefficient (K_{mic}) of 6.30.

บทคัดย่อ

ปาริฉัตร เผ่าดี : การศึกษาวัฏภาคของไมโครอิมันชั้นสำหรับการทำความสะอาคที่ อุณหภูมิต่ำด้วยสารลดแรงตึงผิวชนิดใหม่ (Microemulsion Formulation for Low Temperature Cleaning using Novel Surfactant Systems) อ. ที่ปรึกษา : คร. อัมพิรา เจริญแสง และ Prof. David A. Sabatini 72 หน้า

การศึกษาผงซักฟอกที่เป็นมิตรต่อสิ่งแวดล้อมในอนาคตได้รับความสนใจเนื่องจาก ต้องการลดการใช้พลังงานและอนุรักษ์สิ่งแวคล้อมการออกแบบผงซักฟอกที่มีประสิทธิภาพที่ อุณหภูมิต่ำต้องการผงซักฟอกที่ไม่เพียงมีประสิทธิภาพสูงแต่ยังต้องมีความสามารถสูงในการ ละลายน้ำมันพืชที่สถานะของแข็งที่อุณหภูมิต่ำ หนึ่งในกลไกที่สำคัญในการทำความสะอาคคือ ความสามารถในการละลายของสารลคแรงตึงผิว ดังนั้นงานวิจัยนี้จึงได้ศึกษาความสามารถในการ เกิดไมโครอิมัลชั้นของน้ำมันพืชสำหรับการทำความสะอาด แรงกระทำระหว่างสารลดแรงตึงผิว และน้ำมันถูกศึกษาโดยการเปลี่ยนแปลงวัฏภาคของการเกิดไมโครอิมัลชัน การวัดแรงตึงผิว ระหว่างน้ำมันและสารลดแรงตึงผิว และความสามารถในการละลาย สารลดแรงตึงผิวประจุลบ $[C_{14\cdot15}H_{29\cdot31}$ -(PO) $_8$ -SO $_4$ Na] สารถคแรงคึงผิวไม่มีประจุ $[C_{12\cdot14}H_{27\cdot29}$ -(EO) $_3$ -OH, $C_{12\cdot14}H_{27\cdot29}$ -(EO) $_5$ -OH และ $C_{12-14}H_{27-29}$ -(EO) $_9$ -OH] และสารลดแรงตึงผิวผสมระหว่างประจุลบและ ไม่มีประจุถูก ศึกษาเช่นกัน ปาล์มโอเลอินและปาล์มสเตียรินถูกใช้เพื่อเป็นตัวแทนของน้ำมันที่มีสถานะ ของเหลว และของแข็งตามลำคับ ผลจากงานวิจัยพบว่าการเปลี่ยนแปลงวัฏภาคของไม โครอิมัลชั้น สังเกตได้ยาก พบว่าที่ความเข้มข้นเกลือที่ 4.6% โดยน้ำหนัก ให้ค่าแรงตึงผิวระหว่างสองวัฏภาคที่ ต่ำที่สุดทั้งในสารลดแรงตึงผิวระบบเดี๋ยว [$C_{14-15}H_{29-31}$ -(PO) $_8$ - SO_4Na] และผสม [$C_{14-15}H_{29-31}$ - $(PO)_8$ - $SO_4Na/C_{12-14}H_{27-29}$ - $(EO)_3$ -OH] และจากการศึกษาความสามารถในการละลายปาล์มส เตียรินด้วยสารลดแรงตึงผิวระบบผสม [C₁₄₋₁₅H₂₉₋₃₁-(PO)₈-SO₄Na/C₁₂₋₁₄H₂₇₋₂₉-(EO)₃-OH ที่ 4.6% โดยน้ำหนักเกลือ, 1:1 สัดส่วนโดยโมล] ให้สัดส่วนในการละลายของสารอินทรีย์ในไมเซล ต่อสัคส่วน โมล (MSR) ที่มากที่สุด คือ 0.399 เนื่องจากค่า $X_{\scriptscriptstyle mic}$ (0.29) และ ค่าคงที่ของการละลาย ของสารอินทรีย์จากไมเซล (K_{mic}) เท่ากับ 6.30

ACKNOWLEDGEMENTS

This thesis work is funded by the Petroleum and Petrochemical College; and the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

This research work was partially supported by the Ratchadapisek Sompoch Endowment Fund (2013), Chulalongkorn University (CU-56-900-FC) and Thailand Research Fund (IRG5780012).

This work has been a memorable memory and valuable experience throughout a year-period of research. This work has been successful by many people involved.

The author would like to thank sincerely all of them for supporting and encouraging me to perform this study.

First of all, to say frankly, I would like to thank Dr. Ampira Charoensaeng who provides a valuable advice and support. This thesis would not be success without her professional guidance.

I would like to be obliged Kao Thailand, Bangjak Biofuel and Thai Ethoxylate for assisting in sorbitan surfactants, plam stearin and alcohol ethoxylated surfactants, respectively.

I would like to thank senior students and my friend who gave me advices and their kindness support among experimental period during my study.

This research was conducted under various instrument trainings by staff of the Petroleum and Petrochemical College, with respect they are a valuable person to me.

Finally, I would not have this international experience throughout the M.S. study period without my family's support.

O

TABLE OF CONTENTS

			PAGE
	Title	Page	i
	Abst	ract (in English)	iii
	Abst	ract (in Thai)	iv
	Ackr	nowledgements	V
	Table	e of Contents	vi
	List	of Tables	ix
	List o	of Figures	xi
	Abbr	reviations	xiv
	List	of Symbols	xv
CH	IAPTEI	R	
	I	INTRODUCTION	1
		1.1 Objective	2
		1.2 Scope of Research	3
	II	THEORETICAL BACKGROUND AND LITERATURE	
		REVIEW REFERENCES	4
		2.1 Surfactants	4
		2.1.1 Conventional Surfactants	4
		2.1.2 Extended Surfactants	5
		2.1.3 Renewable-Based Surfactants	6
		2.2 Microemulsion	6
		2.2.1 The Effect of Salinity and Temperature on	
		Microemulsion Formation	8
		2.3 Adsorption at The Liquid-Gas (L/G) and	
		Liquid-Liquid (L/L) Interfaces	10
		2.3.1 The Gibbs Adsorption Equation	10
		2.3.2 Calculation of Effective Area Per Molecule	10

CHAPTER			PAGE
	2.4	Solubilization by Surfactant Solutions	13
		2.4.1. Solubilization in Aqueous Media	14
		2.4.2 Solubilization by Solutions of Surfactants	15
	2.5	Modêl Oil	18
III	EX	PERIMENTAL	26
	3.1	Materials	26
	3.2	Equipment	27
	3.3	Methodology	28
IV	RE	SULTS AND DISCUSSION	31
	4.1	Critical Micelle Concentration (CMC) Measurement	31
		4.1.1 The Effect of NaCl	32
		4.1.2 The Effect of EO Group	33
		4.1.3 The Synergism Effect on Mixed Surfactant Systems	34
	4.2	Effective Area Per Molecule (As)	36
	4.3	Phase Behavior and Microemulsion Formation Study	38
		4.3.1 Microemulsion Phase Behavior and Optimum Salinity	,
		Determination	38
		4.3.2 Effect of Bio-Based Nonionic Surfactants	38
		4.3.3 Effect of EO Group in Nonionic Surfactants	39
		4.3.4 Effect of Mixed Surfactant Systems	39
	4.4	Dynamic Interfacial Tension (IFT) Measurement	40
		4.4.1 Effect of Salinity	40
		4.4.2 Effect of EO Group	42
		4.4.3 Effect of Mixed Surfactant System	42
	4.5	Optimum condition of Palm Stearin (Semi-Solid Fat)	
		Solubilization Study	43
		4.5.1 Effect of Shaking Time	44
		4.5.2 Effect of Salinity	45
		4.5.3 Effect of EO Group	46

CHAPTER		PAGE
	4.5.4 Effect of NaCl in Mixed Surfactant Systems	47
	4.5.5 Effect of Different Surfactant Concentrations	47
	4.6 Semi-Solid Vegetable Oil (Palm Stearin) Solubility Study	48
V	CONCLUSIONS AND RECOMMENDATIONS	52
	5.1 Conclusions	52
	5.2 Recommendations	52
	REFERENCES	53
	APPENDICES	56
	Appendix A Critical Micelle Concentration (CMC)	
	Measurement	56
	Appendix B Hydrophilic-Lipophilic Balance (HLB)	
	Calculation	60
	Appendix C Effective Area Per Molecule (As) Calculation	61
	Appendix D Dynamic Interfacial Tension (IFT) measurement	62
	Appendix E Palm Stearin Solubilization Capacity Calculation	64
	CURRICULUM VITAE	72

LIST OF TABLES

TABLE		PAGE
2.1	The composition of palm stearin and palm olein	19
3.1	Properties of anionic extended and nonionic surfactants	27
4.1	The surface area per molecule as a different surfactant	
	systems	37
4.2	The interaction parameter (β) of mixed surfactant systems by	
	molar ratio	37
4.3	The correlation between β , MSR, and K_{mic}	50
Al	Critical micelle concentration (CMC) of C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -	
	SO ₄ Na with 4.6 %w/v NaCl at 30 °C	56
A2	Critical micelle concentration (CMC) of C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -	
	SO ₄ Na without NaCl added at 30 °C	56
A3	Critical micelle concentration (CMC) of C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₃ -	
	OH without NaCl added at 30 °C	57
A4	Critical Micelle Concentration (CMC) of C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₅ -	
	OH without NaCl added at 30 °C	57
A5	Critical micelle concentration (CMC) of C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₉ -	
	OH without NaCl added at 30 °C	58
A6	Critical micelle concentration (CMC) of mixed surfactant	
	system by 1:1 molar ratio with 4.6 %w/v NaCl at 30 °C	58
A7	Critical micelle concentration (CMC) of mixed surfactant	
	system by 1:1 molar ratio without NaCl added at 30 °C	59
A8	Critical micelle concentration (CMC) of mixed surfactant	
	system by 1:0.1 molar ratio without NaCl added at 30 °C	59
B1	Hydrophilic-Lipophilic Balance (HLB) of each surfactant	66
C1	Surface area per molecule (A _s) of each surfactant system	61
D1	Dynamic interfacial tension (IFT) of C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -SO ₄	
	Na with different NaCl concentrations after 20 min at 30 °C	62

TABLE		
D2	Dynamic interfacial tension (IFT) of C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) _n -OH	
	with different EO groups after 20 min at 30 °C	62
D3	Dynamic interfacial tension (IFT) of mixed surfactant system	62
	(1:1 by molar ratio) after 20 min at 30 °C	63
D4	Dynamic interfacial tension (IFT) of mixed surfactant system	
	(1:0.1 by molar ratio) after 20 min at 30 °C	63
El	Palm stearin removal with different operated time	64
E2	Palm stearin removal with different NaCl concentrations	65
E3	Palm stearin removal with different EO groups in nonionic	
	surfactant $[C_{12-14}H_{25-29}(EO)_n-OH]$	65
E4	Palm stearin removal with different surfactant molar ratios	66
E5	Palm stearin removal with different surfactant [C ₁₄₋₁₅ H ₂₉₋₃₁ -	
	(PO) ₈ -SO ₄ Na] concentrations	66
E6	Palm stearin removal with different surfactant [C ₁₄₋₁₅ H ₂₉₋₃₁ -	
	$(PO)_8$ -SO ₄ Na/C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₃ -OH] concentrations of 1:1 by	
	molar ratio	67
E7	Palm stearin removal with different surfactant [C ₁₄₋₁₅ H ₂₉₋₃₁ -	
	$(PO)_8$ -SO ₄ Na/C ₁₂₋₁₄ H ₂₅₋₂₉ - $(EO)_3$ -OH] concentrations of 1:0.1	o
	by molar ratio	68
E8	Palm stearin solubility of different surfactant [C ₁₄₋₁₅ H ₂₉₋₃₁ -	
	(PO) ₈ -SO ₄ Na] concentrations with 4.6 %w/v NaCl	70
E9	Palm stearin solubility of different surfactant [C ₁₄₋₁₅ H ₂₉₋₃₁ -	
	$(PO)_8$ -SO ₄ Na and $C_{12-14}H_{25-29}$ - $(EO)_3$ -OH] concentrations of	
	1:1 by molar ratio with 4.6 %w/v NaCl	70
E10	Palm stearin solubility of different surfactant [C ₁₄₋₁₅ H ₂₉₋₃₁ -	
	$(PO)_8$ -SO ₄ Na and C ₁₂₋₁₄ H ₂₅₋₂₉ - $(EO)_3$ -OH] concentrations of	
	1:0.1 by molar ratio with 4.6 %w/v NaCl	71

LIST OF FIGURES

FIGURE		PAGE	
2.1	Demonstration of Winsor Type I, III, II, and IV		
	microemulsion.	7	
2.2	Microemulsion phase map. The solid line indicates the		
	different microemulsion types (I, III, II, and IV). The inset		
	figures show the changes in curvature as the microemulsion		
	transition from Type I to Type III to Type II microemulsion.	8	
2.3	The effect of molecular environmental conditions on		
	interfacial tension and phase volume. Shaded phases indicate		
	surfactant locations.	10	
2.4	The surface tension (γ)versus surfactant concentration ($\log C_1$).	12	
2.5	The solubility as a function of surfactant concentration.	14	
2.6	The location of solubilizate in a surfactant micelle.	15	
4.1	The determination of critical micelle concentration (CMC).	31	
4.2	The CMC values of $C_{14-15}H_{29-31}$ -(PO) ₈ -SO ₄ Na with and without		
	added.	32	
4.3	The CMC values of mixed surfactant system between C ₁₄₋₁₅		
	$H_{29\text{-}31}\text{-}(PO)_8\text{-}SO_4Na$ and $C_{12\text{-}14}H_{25\text{-}29}\text{-}(EO)_3\text{-}OH,\ 1:1$ by molar		
	ratio with and without NaCl added.	33	
4.4	The CMC values of $C_{12-14}H_{25-29}$ -(EO) _n -OH with different EO		
	groups.	34	

LIST OF FIGURES

FIGURE			. PAGE	
	4.5	The CMC values of different surfactant systems without NaCl		
		added.	35	
	4.6	The CMC values of different surfactant systems with NaCl		
		added.	35	
	4.7	The microemuslion phase behavior of different surfactant		
		formulation. a) $C_{14-15}H_{29-31}$ -(PO) ₈ -SO ₄ Na with different NaCl		
		concentration, b) $[C_{12-14}H_{25-29}-(EO)_n-OH (n = 3, 5, and 9)], c)$		
		SO and mixed surfactant systems [$C_{14-15}H_{29-31}$ -(PO) ₈ -SO ₄ Na		
		and SO] and d.) mixed surfactant systems [$C_{14-15}H_{29-31}$ -(PO) ₈ -		
		SO_4Na and $C_{12-14}H_{25-29}$ -(EO) ₃ -OH] with different molar ratios.		
		All systems were kept under the same condition at 30 °C.	40	
	4.8	Dynamic interfacial tension as a function of NaCl		
		concentration (salinity scan) for 0.0005 M $C_{14-15}H_{29-31}$ -(PO) ₈ -		
		SO ₄ Na with palm olein after 20 min.	41	
	4.9	Dynamic interfacial tension as a function of number of EO		
		group for 0.0005 M $C_{12-14}H_{25-29}$ -(EO) _n -OH (n = 3, 5, and 9)		
		with palm olein.	42	
	4.10	Dynamic interfacial tension as of 0.05 M C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -		
		SO ₄ Na/C ₁₂₋₁₄ H ₂₅₋₂₉ -(EO) ₃ -OH with and without NaCl added		
		with palm olein after 20 min.	43	
	4.11	The percentage of oil removal as a function of time at 0.05M		
		$C_{14-15}H_{29-31}$ -(PO) ₈ -SO ₄ Na.	44	
	4.12	The percentage of oil removal at different NaCl		
		concentrations with 0.05 M C ₁₄₋₁₅ H ₂₉₋₃₁ -(PO) ₈ -SO ₄ Na.	45	

LIST OF FIGURES

FIGURE		PAGE
4.13	The percentage of palm stearin removal with different EO	
	groups in nonionic surfactants.	46
4.14	The percentage of palm stearin removal with different	
	surfactant ratios and NaCl concentrations.	47
4.15	The surfactant concentration (M) versus palm stearin (semi-	
	solid fat) solubility (M).	48
4.16	The solubility versus surfactant concentration. All	
	experiments were performed at 30 ± 1 °C.	50

Abbreviations

PO Polypropylene oxide

EO Polyethylene oxide

SS Sorbitan stearate

SO Sorbitan oleate

CMC Critical micelle concentration

IFT Interfacial tension

HLB Hydrophilic-Lipophilic balance

MSR Molar solubilization ratio

X_a Mole fraction of organic in micelle-free aqueous phase

X_{mic} Mole fraction of organic in micelle pseudophase

K_{mic} Micelle-water partition coefficient

List of Symbols

3	Interaction parameter
A_s	Effective area per molecule
X	Mole fraction of component in mixed surfactant solution
a	Mole fraction of surfactant in total concentration
S*	Optimum salinity
r	Surfactant tension