

**RHEOLOGICAL AND OPTICAL PROPERTIES OF CATIONIC
SURFACTANTS-FATTY ALCOHOL EMULSIONS**

Ms.Siriluck Suksamranchit

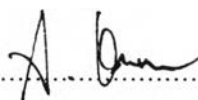
A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
and Case Western Reserve University

2000


ISBN 974-334-150-1


Thesis Title : Rheological and Optical Properties of Cationic
Surfactants-Fatty Alcohol Emulsions
By : Ms. Siriluck Suksamranchit
Program : Petrochemical Technology
Thesis Advisors : Assoc. Prof. Anuvat Sirivat

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


..... College Director
(Prof. Somchai Osuwan)

Thesis Committee:


.....
(Assoc. Prof. Anuvat Sirivat)


.....
(Dr. Nantaya Yanumet)


.....
(Dr. Pitt Supaphol)

ABSTRACT

4171028063: PETROCHEMICAL TECHNOLOGY PROGRAM

KEYWORD: Cetyltrimethyl Ammonium Chloride/ CTAC/

Behenyltrimethyl Ammonium Chloride/ BTAC/Fatty

Alcohol/FA/ Hydroxyethyl Cellulose/ HEC/ Emulsion.

Siriluck Suksamranchit: Rheological and optical properties of cationic surfactants-fatty alcohol emulsions. Thesis

Advisor: Assoc. Prof. Anuvat Sirivat, 114 pp

ISBN 974-334-150-1

Rheological and optical properties of cationic surfactants (CTAC and BTAC) and fatty alcohol (FA) emulsions were investigated in terms of fatty alcohol concentration, temperature and pH. Entanglement storage modulus (G_N^0), Bingham stress (τ_B) and zero shear viscosity (η_0) increased with fatty alcohol content for both CTAC/FA and BTAC/FA systems. In the CTAC/FA system, the vesicle structure changed to the binding lamellar structure whereas in the BTAC/FA system, the vesicle structure changed to the sunflower-like structure as the proportion of fatty alcohol increased. Values of G_N^0 , τ_B and η_0 at high fatty alcohol concentrations were independent of temperature. The pH did not affect G_N^0 , τ_B and η_0 at all fatty alcohol concentrations in both CTAC/FA and BTAC/FA systems as can be seen from the unchanged lamellar structure. The effect of annealing temperature was studied in CTAC/FA/HEC and BTAC/FA/HEC systems. After annealing at 40 and 53°C, G_N^0 and η_0 recovered to their initial values within 1 day; the lamellar structure also recovered. However, at 80°C, G_N^0 and η_0 showed drastic decreases due to the formation of optically isotropic oil-in-water emulsions.

บทคัดย่อ

ศิริลักษณ์ สุขสำราญจิตต์ : สมบัติการไหลและโครงสร้างของอิมัลชันระหว่างสารลดแรงตึงผิวประเภทประจุบวกและอัลกอฮอล์ชนิดไขมัน (Rheological and optical properties of cationic surfactants- fatty alcohol emulsions) อ. ที่ปรึกษา : รศ.ดร. อนุวัฒน์ ศิริวัฒน์ 114 หน้า ISBN 974-334-150-1

สมบัติการไหลและโครงสร้างของอิมัลชันของสารลดแรงตึงผิวประเภทประจุบวก (CTAC และ BTAC) และอัลกอฮอล์ชนิดไขมันถูกศึกษาในเรื่องของความเข้มข้นของอัลกอฮอล์ชนิดไขมัน อุณหภูมิ และ ค่าความเป็นกรด-เบส ในระบบ CTAC/FA และ ระบบ BTAC/FA เมื่อความเข้มข้นของอัลกอฮอล์ชนิดไขมันเพิ่มขึ้น ค่ามอดูลัสสะสม ณ จุด พัวพัน ค่าแรงบึงแสม และ ค่าความหนืดจะเพิ่มขึ้น ในระบบ CTAC/FA โครงสร้างแบบเวสทิเคิล (vesicle) จะเปลี่ยนเป็นโครงสร้างแบบลามลลาแบบกลุ่ม (lamellar) ในขณะที่ในระบบ BTAC/FA โครงสร้างแบบเวสทิเคิลจะเปลี่ยนเป็นโครงสร้างแบบดอกทานตะวัน (sunflower-like) เมื่อความเข้มข้นของอัลกอฮอล์ชนิดไขมันเพิ่มขึ้น ค่ามอดูลัสสะสม ณ จุด พัวพัน ค่าแรงบึงแสม และ ค่าความหนืดที่ความเข้มข้นของอัลกอฮอล์ชนิดไขมันสูงจะไม่เปลี่ยนแปลงตามอุณหภูมิ ค่าความเป็นกรด-เบส ไม่มีผลต่อค่ามอดูลัสสะสม ณ จุด พัวพัน ค่าแรงบึงแสม และ ค่าความหนืดที่ทุกความเข้มข้นของอัลกอฮอล์ชนิดไขมันทั้งระบบ CTAC/FA และระบบ BTAC/FA ซึ่งเห็นได้จากโครงสร้างลามลลาที่ไม่เปลี่ยนแปลง ในการวิเคราะห์ถึงผลของการให้ความร้อนกับอิมัลชันในระบบ CTAC/FA/HEC และระบบ BTAC/FA/HEC ค่ามอดูลัสสะสม ณ จุด พัวพัน และ ค่าความหนืด สามารถกลับสู่ค่าเริ่มต้นภายใน 1 วันพร้อมกับโครงสร้างลามลลาจะกลับสู่โครงสร้างแบบเดิม อย่างไรก็ตามที่ 80 องศาเซลเซียส ค่ามอดูลัสสะสม ณ จุด พัวพัน และ ค่าความหนืดลดลงมากเนื่องจากเกิดอิมัลชันแบบน้ำมันในน้ำ

ACKNOWLEDGEMENTS

This thesis could not have been completed without the participation of the following individuals and organizations. The author would like to thank all of people for making this work possible.

The author would like to gratefully acknowledge all professors who have taught her at the Petroleum and Petrochemical College, Chulalongkorn University. The author greatly appreciates Associate Professor Anuvat Sirivat for his valuable suggestions, constructive criticism and proof-reading of this thesis and manuscript. The author would like to give special thanks to BIOTEC for allow her to use optical microscope. The author would like to give thanks to Mr. Amnuay Jintasirikul for training in the optical microscope. The author appreciates the Unilever Thai Holding Co., Ltd. for raw materials support. The author would like to give thanks to Dr. Nantaya Yanumet and Dr. Pitt Supaphol for being thesis committee members.

The author thanks Mr. Tanapatr Bameesangpet for training on the experimental techniques and giving the knowledge needed for this work. The author also thanks all of her friends who encouraged her in carrying out the experiment and Petroleum and Petrochemical College staffs for their help.

Finally, the author is deeply indebted to her family for their great love, understanding encouragement, and for constant everlasting source of her inspiration.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	x
List of Figures	xi
CHAPTER	
I	
INTRODUCTION	1
1.1 Background	1
1.2 Cosmetics Emulsion	1
1.2.1 Definition of Emulsion (IUPAC, 1972)	1
1.2.2 Emulsifying Agents or Surfactants	2
1.2.3 The Shape of Micelles in Solution	3
1.2.4 Emulsion Stability	4
1.2.5 Liquid Crystal Stabilization	5
1.2.6 Vesicles and Liposomes	6
1.3 Major Raw Materials in Hair-Care Product	6
1.3.1 Cationic Surfactants	6
1.3.2 Fatty Alcohol	8
1.3.3 Water Soluble Polymer	8
1.4 Rheology of Cosmetics Emulsion	8
1.5 Factors Influencing the Rheological Behavior of Emulsions	10

CHAPTER	PAGE
1.6 Applications	11
1.7 Objectives	12
1.8 Scope of Work	12
II LITERATURE SURVEY	13
III EXPERIMENTAL	20
3.1 Materials	20
3.1.1 Cetyltrimetyl Ammonium Choride (CTAC)	20
3.1.2 Behenyltrimetyl Ammonium Choride (BTAC)	20
3.1.3 Fatty Alcohol (FA)	21
3.1.4 Hydroxyethyl Cellulose (Natrasol) (HEC)	21
3.1.5 Deionized Distilled Water	22
3.2 Equipment	22
3.2.1 Laser Scanning Microscope (LSM)	22
3.2.2 Rheometer	24
3.2.2.1 Steady State Method	25
3.2.2.2 Dynamic Method	25
3.3 Experimental Conditions	26
3.3.1 Conditions in Microscope Measurement	26
3.3.2 Conditions in Oscillatory Measurements	26
3.3.2.1 Dynamic Strain Sweep Default Test	26
3.3.2.2 Dynamic Frequency Sweep Default Test	27
3.3.3 Conditions in Steady Shear Measurement (Steady Rate Sweep Test)	28
3.4 Data Analysis	28

CHAPTER		PAGE
	3.5 Methodology	29
	3.5.1 Sample Preparation of Emulsion of CTAC/FA	29
	3.5.2 Sample Preparation of Solution of HEC	30
	3.5.3 Sample Preparation of Emulsion of CTAC/FA/HEC	31
	3.5.4 Sample Preparation of Emulsion of BTAC/FA	32
	3.5.5 Sample Preparation of Emulsion of BTAC/FA/HEC	33
	3.5.6 Sample Preparation of Emulsion for Studying Effect of Annealing	34
	3.5.6 Sample Preparation of Emulsion for Studying Effect of Temperature	35
	3.5.7 Sample Preparation of Emulsion for Studying Effect of pH	35
IV	RESULTS AND DISCUSSION	36
	4.1 Effect of Fatty Alcohol Concentration	38
	4.2 Effect of Temperature	44
	4.3 Effect of Annealing Temperature	48
	4.3.1 CTAC/FA/HEC Emulsions	48
	4.3.2 BTAC/FA/HEC Emulsions	59
	4.4 Effect of pH	70
V	CONCLUSIONS AND RECOMMENDATIONS	80
	5.1 Conclusions	80
	5.1.1 Effect of Fatty Alcohol Concentration	80

CHAPTER	PAGE
5.1.2 Effect of Temperature	80
5.1.3 Effect of Annealing Temperature	80
5.1.4 Effect of pH	81
5.2 Recommendations	81
REFERENCES	82
APPENDICES	86
CURRICULUM VITAE	114

LIST OF TABLES

TABLE		PAGE
1.1	The Structure of Micelles at Various Geometrical Packing	3
4.1	Effect of Fatty Alcohol Concentration	36
4.2	Effect of Temperature	36
4.3	Effect of Annealing Temperature	37
4.4	Effect of pH	37

LIST OF FIGURES

FIGURE	PAGE
1.1 Schematic drawing of the structure of (a) hexagonal phase and (b) lamellar phase.	4
1.2 Schematic drawing of the structure of (a) vesicles structure and (b) liposomes phase.	6
1.3 Various types of fluid characteristics.	9
3.1 The chemical structure of CTAC.	20
3.2 The chemical structure of BTAC.	21
3.3 The chemical structure of Hydroxyethyl Cellulose.	22
3.4 The general view of the LSM system.	23
3.5 The cone and plate rheometer.	24
4.1 G_N^0 vs. fatty alcohol concentration of the CTAC/FA and BTAC/FA emulsions at equilibrium.	40
4.2 τ_B vs. fatty alcohol concentration of the CTAC/FA and BTAC/FA emulsions at equilibrium.	40
4.3 η_o vs. fatty alcohol concentration of the CTAC/FA and BTAC/FA emulsions at equilibrium.	41
4.4 Micrographs of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium: (a) CTAC/FA = 1.0/1.0; (b) CTAC/FA = 1.0/2.0; (b) CTAC/FA = 1.0/4.0; (d) CTAC/FA = 1.0/5.0; (e) CTAC/FA = 1.0/6.0 and (f) CTAC/FA 1.0/8.0.	42

FIGURE	PAGE
4.5 Micrographs of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium: (c) CTAC/FA = 1.0/1.0; (b) CTAC/FA = 1.0/2.0; (d) CTAC/FA = 1.0/4.0; (d) CTAC/FA = 1.0/5.0; (e) CTAC/FA = 1.0/6.0 and (f) CTAC/FA 1.0/8.0	43
4.6 G_N° vs. temperature of CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	45
4.7 G_N° vs. temperature of BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	45
4.8 τ_B vs. temperature of CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	46
4.9 τ_B vs. temperature of BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	46
4.10 η_o vs. temperature of CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	47
4.11 η_o vs. temperature of BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	47
4.12 G_N° vs. aging time of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.	50
4.13 G_N° vs. aging time of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.	50
4.14 τ_B vs. aging time of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.	51
4.15 τ_B vs. aging time of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.	51

FIGURE	PAGE
4.16 η_o vs. aging time of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.	52
4.17 η_o vs. aging time of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.	52
4.18 Micrographs of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 40°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	53
4.19 Micrographs of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 53°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	54
4.20 Micrographs of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 80°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	55
4.21 Micrographs of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 40°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	56
4.22 Micrographs of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 53°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	57

FIGURE	PAGE
4.23 Micrographs of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 80°C at various aging times. (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	58
4.24 G_N^0 vs. aging time of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.	61
4.25 G_N^0 vs. aging time of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.	61
4.26 τ_B vs. aging time of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.	62
4.27 τ_B vs. aging time of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.	62
4.28 η_O vs. aging time of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.	63
4.29 η_O vs. aging time of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.	63
4.30 Micrographs of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 40°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	64
4.31 Micrographs of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 53°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	65

FIGURE	PAGE
4.32 Micrographs of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 80°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	66
4.33 Micrographs of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 40°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	67
4.34 Micrographs of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 53°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days; (d) aging 14 days.	68
4.35 Micrographs of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 80°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.	69
4.36 G_N^0 vs. pH of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	71
4.37 G_N^0 vs. pH of the BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	71
4.38 τ_B vs. pH of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	72
4.39 τ_B vs. pH of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	72
4.40 η_O vs. pH of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	73

FIGURE	PAGE
4.41 η_o vs. pH of the BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.	73
4.42 Micrographs of the CTAC/FA = 1.0/2.0 emulsions at various pH: (a) pH 3 (b) pH 5 (c) pH 7 and (d) pH 9.	74
4.43 Micrographs of the CTAC/FA = 1.0/4.0 emulsions at various pH: (a) pH 3 (b) pH 5 (c) pH 7 and (d) pH 9.	75
4.44 Micrographs of the CTAC/FA = 1.0/6.0 emulsions at various pH: (a) pH 3 (b) pH 5 (c) pH 7 and (d) pH 9.	76
4.45 Micrographs of the BTAC/FA = 1.0/2.0 emulsions at various pH: (a) pH 3 (b) pH 5 (c) pH 7 and (d) pH 9.	77
4.46 Micrographs of the BTAC/FA = 1.0/4.0 emulsions at various pH: (a) pH 3 (b) pH 5 (c) pH 7 and (d) pH 9.	78
4.47 Micrographs of the BTAC/FA = 1.0/6.0 emulsions at various pH: (a) pH 3 (b) pH 5 (c) pH 7 and (d) pH 9.	79