

**ASPECT OF IONIC POLYMER/OPPOSITELY CHARGED SURFACTANT
COMPLEX**

Ratana Giles

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

2006

ISBN 974-9990-01-3

Thesis Title: Aspect of Ionic Polymer/Oppositely Charged Surfactant Complex
By: Ratana Giles
Program: Polymer Science
Thesis Advisors: Asst. Prof. Manit Nithitanakul
Assoc. Prof. Rathanawan Magaraphan
Prof. John F. Scamehorn

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

..... *Nantaya Yanumet* College Director
(Assoc. Prof. Nantaya Yanumet)

Thesis Committee:

..... *MN*
(Asst. Prof. Manit Nithitanakul)

..... *R. Magaraphan*
(Assoc. Prof. Rathanawan Magaraphan)

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

..... *Hathaikarn Manuspiya*
(Dr. Hathaikarn Manuspiya)

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

ABSTRACT

4772021063: Polymer Science Program

Ratana Giles: Aspect of Ionic Polymer/Oppositely Charged
Surfactant Complex

Thesis Advisors: Asst.Prof. Manit Nithitanakul, Assoc.Prof.

Rathanawan Magaraphan and Prof. John F. Scamehorn 80 pp. ISBN
974-9990-01-3

Keywords: Polymer-surfactant interaction/ Phase diagram/Surface tension/
Electrophoretic mobility/ Tribology/ Friction

It is widely known that a solution of oppositely charged polymer and surfactant interact strongly before potentially separating into a dilute phase and a phase concentrated in both polymer and surfactant. The phase separation process is the result of flocculation followed by sedimentation. This study focuses on one commercial application of polymer-surfactant flocculation; 2 in 1 hair shampoos containing anionic surfactant, sodium lauryl ether sulphate (SLES) and cationic polymer, guar hydroxypropyltrimonium chloride (Jaguar). Polymer-surfactant interactions were studied by surface tension measurements and results show that the surface tension was reduced when Jaguar was added. Additionally, a phase diagram was constructed to identify the precipitation phase boundary. This boundary is believed to be driven by two factors: the concentration of the key ingredients and the kinetics of flocculation. The flocs in the phase precipitation zone were characterized by several techniques, including the dry weight of floc, particle size, electrophoretic mobility, chemical composition and morphology. It is argued that the physiochemical properties of the precipitates is governed by two factors: bulk chemical composition and kinetics of flocculation. Moreover, the inter-relationship between the various physiochemical properties was investigated, for example, results suggest a strong relationship between electrophoretic mobility and chemical composition. The effect of floc composition on frictional properties of hair was determined. Hair friction was found to be dependent on particle charge.

บทคัดย่อ

นางรัตนา ไกลส์: การศึกษาคุณสมบัติของสารประกอบซับซ้อนของโพลิเมอร์ที่ประจุกับสารซักล้างที่ประจุตรงกันข้าม (Aspect of Ionic Polymer/Oppositely Charged Surfactant Complex) อาจารย์ที่ปรึกษา: ผศ. ดร. มานิตย์ นิธิธนากุล, รศ.ดร. รัตนวรรณ มกรพันธุ์ และ ศ.ดร. จอห์น เอฟ สแกมฮอร์น 80 หน้า ISBN 974-9990-01-3

เป็นที่รู้จักกันอย่างกว้างขวางว่าในสารละลายของโพลิเมอร์ที่มีประจุกับสารลดแรงตึงผิวที่มีประจุตรงกันข้าม จะเกิดปฏิกิริยาต่อกันอย่างเข้มข้นก่อนที่จะนำไปสู่การแยกสถานะเพื่อเข้าสู่สถานะที่เจือจาง และสถานะที่เข้มข้นไปด้วยส่วนประกอบที่มีทั้งโพลิเมอร์ และสารลดแรงตึงผิว ขบวนการของสถานะที่เกิดการแยก เป็นผลมาจากขบวนการที่เรียกว่าฟลอคคูเลชันตามด้วยการตกตะกอน ในการวิจัยครั้งนี้มุ่งที่จะศึกษาการประยุกต์ใช้คุณสมบัติของฟลอคคูเลชัน จากการทำปฏิกิริยาของโพลิเมอร์ และสารลดแรงตึงผิวในแชมพูสระผมที่มีส่วนประกอบของสารลดแรงตึงผิวประเภทคือ โซเดียม ลอริล อีเธอร์ ซัลเฟต (SLES) และโพลิเมอร์ที่มีประจุบวก กัวไฮดรอกซีโพรพิล ไตรโมเนียม คลอไรด์ (Jaguar) การศึกษาการทำปฏิกิริยาระหว่างโพลิเมอร์ และสารลดแรงตึงผิวทำโดยการวัดค่าแรงตึงผิวของสารละลาย ซึ่งพบว่าตัวอย่างที่มีการเติมโพลิเมอร์ให้ค่าแรงตึงผิวที่น้อยกว่าตัวอย่างที่มีสารลดแรงตึงผิวเพียงอย่างเดียว นอกจากนี้ได้มีการศึกษาเฟสไดอะแกรมเพื่อบอกถึงขอบเขตของสถานะที่เกิดการตกตะกอน ซึ่งจากการทดลองน่าจะเชื่อได้ว่าขอบเขตของการตกตะกอนนี้ถูกผลักดันจากปัจจัย 2 อย่างคือ ความเข้มข้นของสารสำคัญทั้งสองชนิดและจลนศาสตร์ของการเกิดฟลอคคูเลชัน คุณลักษณะของอนุภาคที่จับกันเป็นกลุ่มก้อนที่เกิดขึ้นในสถานะที่เกิดการตกตะกอนได้ถูกศึกษาโดยเทคนิคต่างๆ ทั้งนี้รวมถึงน้ำหนักของสารที่แห้ง ขนาดอนุภาค การเคลื่อนไหวในสนามไฟฟ้า ส่วนประกอบทางเคมี และลักษณะโครงสร้าง ซึ่งพบว่าคุณสมบัติทางกายภาพและเคมี น่าจะถูกควบคุมโดยปัจจัย 2 อย่างคือส่วนประกอบทางเคมีของสารและจลนศาสตร์ของการเกิดฟลอคคูเลชัน นอกจากนี้ได้มีการศึกษาผลของส่วนประกอบของอนุภาคที่จับกันเป็นกลุ่มก้อนที่มีต่อคุณสมบัติในการลดแรงเสียดทานของผม ซึ่งพบว่าคุณสมบัติดังกล่าวขึ้นอยู่กับประจุของอนุภาค

ACKNOWLEDGEMENTS

This thesis work is partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium). I would like to thank The Petroleum and Petrochemical College, Chulalongkorn University where I have gained superior knowledge in polymer science.

I also would like to acknowledge GTC, Unilever Thai trading Ltd. for their support in supplying materials for this study, especially Ms.Jaruwan Saktavornlert who helped in friction measurements and Ms.Boonsom Naktham who helped prepare the hair switches for the whole study. Moreover, I would also like to thank Dr. David Birtwistle, Dr. Anuchai Sinsawat and Dr. Colin Giles for their invaluable discussion and advice.

I would like to express grateful appreciation to Asst. Prof. Manit Nithitanakul, Assoc. Prof. Rathanawan Magaraphan and Prof. John F. Scamehorn for their useful discussion and recommendation. I would also like to thank Dr. Hathaikarn Manuspiya and Assoc. Prof. Sumaeth Chavadej for their role in the thesis committee.

I gratefully appreciate all faculties and staff at The Petroleum and Petrochemical College for their assistance in making my work a success. I would also like to thank all of my friends for their support, cheerfulness and helpfulness.

I am especially indebted to Unilever Thai Trading Ltd for providing financial support for my 2-year study at the college.

Finally, I would like to express my deepest gratitude to my family for their forever love and understanding. Special thanks to my husband for his truly patience, understanding and encouragement.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	iv
List of Figures	x
 CHAPTER	
I INTRODUCTION	1
 II THEORITICAL BACKGROUND AND LITERARURE REVIEW	 3
2.1 The Theory of Flocculation and Floc Characterization	3
2.2 The Principals of Friction and its Measurement	11
 III EXPERIMENTAL	 17
3.1 Materials	17
3.2 Methodology	19
3.2.1 Surface Tension	18
3.2.2 Phase Diagram	18
3.2.3 Weight Measurement and Composition of flocs	18
3.2.4 Size Distribution of Floc	19
3.2.5 Electrophoresis Mobility	20
3.2.6 Surface Analysis	22
3.2.6.1 Friction Measurement	22
3.2.6.2 Friction as a Function of Applied Floc mass	23
3.2.6.3 Friction under Constant Floc Mass	24

CHAPTER	PAGE
IV RESULTS AND DISCUSSION	25
PART I: Characterisation of Cationic Guar/SLES aggregate	25
4.1 Introduction	25
4.2 Characterisation of the Cationic guar/SLES system	26
4.2.1 Surface Tension Measurements	26
4.2.2 Phase Diagram of Cationic guar/SLES	30
4.3 Characterisation of the Aqueous Dispersion of Cationic guar/SLES Aggregates	35
4.3.1 Floc Size Determination	35
4.3.2 Determination of Floc Electrophoretic Mobility	40
4.4 Characterisation of Isolated, Dry Cationic guar/ SLES Aggregates	43
4.4.1 Determination of Weight of Dry Extracted Floc	43
4.4.2 Chemical Composition Determination by FTIR	46
4.4.3 Determination of Chemical Composition: Sulphur/Nitrogen ratio	47
4.4.4 Determination of Floc Topography: SEM Sulphur/Nitrogen ratio	49
4.4.4.1 Effect of Drying Method	49
4.4.4.2 Effect of Agitation Speed	50
4.4.4.3 Effect of Polymer Content	51
4.5 Inter-relationships Between Different Characteristics	53
4.5.1 Floc Size and Floc Charge	53
4.5.2 Floc Size and Weight Dry Floc	54
4.5.3 Floc Size and Chemical composition	55
4.5.4 Floc Charge and Dry Weight of Isolated Floc	56
4.5.5 Floc Charge and Chemical Composition	57

PART II: The Influence of Floc Characteristics on Frictional Properties	59
4.6 Introduction	59
4.7 Friction as a Function of Applied Floc Mass	59
4.8 Friction as a Function of Floc Characteristic under Constant Floc Mass	61
4.8.1 Relationship of Friction of Treated Hair Fibres and Chemical Composition of Bulk	62
4.8.2 Relationship of Friction of Treated Hair Fibres and Characterization of Floes	64
V CONCLUSIONS	66
REFERENCES	69
APPENDICES	72
Appendix A Visual Appearance	72
Appendix B Equilibrium pH of Studied Points in Phase Diagram	72
Appendix C Correlation Coefficient Test (Person's)	73
Appendix D Method for Hair Switch Preparation and Cleaning	74
Appendix E Hair Surface Morphology by AFM	75
CURRICULUM VITAE	80

LIST OF TABLES

TABLE		PAGE
4.1	Value of the CFC and CRC for different systems of cationic polymer, Jaguar C13S, and anionic surfactant, SLES	31
4.2	Composition of liquor used to make the flocs for future studies	34

LIST OF FIGURES

FIGURE	PAGE
1.1 Conditions in bulk and surface of solution containing a polycation	5
1.2 Region of hydrodynamic and boundary lubrications	13
1.3 Cross-sectional schematic of a human hair fiber	14
1.4 Frictional curve of human hair treated with Polymer JR-400 against a capstan at wet in water	15
1.5 Photograph and schematic of frictional hysteresis apparatus based upon Texture analyzer	16
1.3 Cross-sectional schematic of a human hair fiber	14
1.4 Frictional curve of human hair treated with Polymer JR-400 against a capstan at wet in water	15
1.5 Photograph and schematic of frictional hysteresis apparatus based upon Texture analyzer	16
3.1 Structure of sodium lauryl ether sulfate consist of C12 chain length with average one ethoxylation ($n=1$)	17
3.2 Structure of cationic Jagaur	17
3.3 Properties of the scattered light	20
3.4 Diagram of electrical double layer	20
3.5 Typical friction hyteresis plot	23
4.1 Surface tension measurements of an SLES solution at 30 ± 1 °C	26
4.2 Surface tension measurements of SLES/cationic guar mixtures as a function of SLES concentration, at 30 ± 1 °C	28
4.3 Phase diagram for solution of cationic polymer, Jaguar C13S, and anionic surfactant, SLES	30

FIGURE	PAGE
4.4 Phase diagram of the Jaguar C13/SLES system obtained during this study. Highlighting the 8 points to be used for further study	33
4.5 A photograph highlighting the differences in the appearance of the flocs and supernatants produced from the eight points in the phase diagram	34
4.6 Particle size distribution profiles for flocs produced at different points in the phase diagram	35
4.7 Floc median particle size as a function of polymer concentration for two different surfactant concentrations (1mM & 30mM) as measured at a constant floc age (10mins)	36
4.8 Floc median particle size as a function of surfactant concentration for three different polymer concentrations (0.2, 0.5 & 1.0g/l) as measured at a constant floc age (10mins)	37
4.9 Floc median size at a constant polymer/surfactant ratio, expressed as relative dilution as measured at a constant floc age (10mins)	39
4.10 Electrophoresis mobility as a function of polymer concentration for two different level of surfactant solution	40
4.11 Electrophoresis mobility as a function of surfactant concentration for three different levels of polymer concentration at 0.2, 0.5 and 1 g/l.	42
4.12 Electrophoresis mobility as a function of relative dilution	43
4.13 Dry weight of isolated floc from selected points in the precipitated, two phase region for different polymer concentrations as a function of surfactant concentration	44

FIGURE		PAGE
4.14	Weight of dried floc extract as a function of polymer concentration for a given surfactant concentration	45
4.15	FTIR spectra of pure cationic guar polymer Jaguar C13S, pure anionic surfactant, SLES and extracted dry flocs	46
4.16	Sulphur/Nitrogen ratio of dried, isolated flocs as a function of surfactant concentration for constant polymer concentrations	47
4.17	Sulphur/Nitrogen ratio of dried, isolated flocs as a function of polymer concentration for constant surfactant concentration	49
4.18	A Typical structure of flocs after freeze drying	50
4.19	The structure of flocs after oven drying under vacuum at 40°C	50
4.20	Floc morphologies identified by SEM prepared by freeze drying at different agitation speed	51
4.21	Flocs prepared by freeze drying and studied by SEM as function of polymer concentration	52
4.22	Median Particle Size as a function of electrophoretic mobility	53
4.23	Graphs examining the inter-relationship between weight of extracted dry floc and particle size	54
4.24	inter-relationship between floc size and floc chemical composition	55
4.25	Relationship between electrophoretic mobility and weight of dry extract of floc for the two different surfactant levels	56

FIGURE	PAGE
4.26 The relationship between electrophoretic mobility and chemical composition of the floc (S/N ratio)	57
4.27 Change in Frictional forces on hair switches as a function of different floc loading	60
4.28 Relationship between wet and dry friction for the eight compositions, conducted under constant floc mass	61
4.29 Relationship between wet and dry friction with varying polymer concentrations	62
4.30 Relationship between wet and dry friction with varying surfactant concentrations	63
4.31 Wet and Dry friction as a function of Electrophoresis mobility of the pre-prepared flocs	64
4.32 Wet and Dry friction as a function of the chemical composition of the pre-prepared flocs as determined by the S/N ratio	65