PHYSICAL AND RHEOLOGICAL PROPERTIES OF NONIONIC POLYMERS - IONIC SURFACTANTS COMPLEXES

Ms. Khine Yi Mya

A Dissertation Submitted in Partial Fulfillment 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
2002

ISBN 974-03-1553-4

Thesis Title	:	Physical and Rheological Properties of Nonionic Polymers – Ionic Surfactants Complexes
By	:	Khine Yi Mya
Program	:	Polymer Science
Thesis Advisors	:	Assoc. Prof. Anuvat Sirivat Prof. Alexander M. Jamieson

---

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

K. Bunyakiat.
..... College Director
(Assoc. Prof. Kunchana Bunyakiat)

Thesis Committee:

K. Bunyakiat.
.....(Chairman)
(Assoc. Prof. Kunchana Bunyakiat)

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

.....
(Prof. Alexander M. Jamieson)

Nantaya Yanumet
.....
(Asst. Prof. Nantaya Yanumet)

Asira Fuongfuchat
.....
(Dr. Asira Fuongfuchat)

ABSTRACT

4092002063 : POLYMER SCIENCE PROGRAM

Khine Yi Mya: Physical and Rheological Properties of Nonionic Polymers - Ionic Surfactants Complexes.

Thesis Advisors: Prof. Alexander M. Jamieson and Assoc. Prof. Anuvat Sirivat, 376 pp. ISBN 974-03-1553-4

Keywords : Polyethylene oxide/ PEO/ Hexadecyltrimethylammonium chloride/ HTAC/ Hydroxypropyl cellulose/ HPC/ Cocamidopropyl dimethyl glycine/ CADG/ Conductivity/ Viscosity/ Dynamic light scattering/ DLS/ Static light scattering/ SLS/ Refractive index increment/ Dialysis equilibrium

The formation of a polymer-surfactant complex upon mixing a nonionic polymer, poly(ethylene oxide) (PEO), with a cationic surfactant, hexadecyltrimethylammonium chloride (HTAC), was studied by observing the changes in conductivity, specific viscosity (η_{sp}), and hydrodynamic radius (R_h). The conductivity data showed that an interaction between PEO and HTAC occurred at a temperature above 25 °C, as indicated by a decrease in the critical aggregation concentration in the presence of PEO relative to the critical micelle concentration of a surfactant in the absence of PEO. The binding of HTAC to PEO induced a chain expansion due to electrostatic repulsions between bound micelles. On further addition of HTAC, η_{sp} and R_h reached a maximum at the saturation of binding, and then decreased because of the contraction of the PEO-HTAC complex due to electrostatic screening from the accumulation of free micelles and counterions in the solution.

From the static light scattering, the structures of PEO-HTAC complexes were determined by means of molecular weight measurement at different concentration ratios of HTAC to PEO. Multichain complexation was observed in aqueous solution in the formation of the complex at the maximum binding. However, in the presence of 0.1 M KNO_3, the structure of the complex changed from

multichain to unipolymer complexation. Moreover, the number of bound HTAC molecules per PEO chain increased from 0.12 mole HTAC per mole EO to 0.23 mole HTAC per mole EO in salt solution.

Rheological measurements also indicated that the storage modulus G' and the loss modulus G" of the concentrated PEO-HTAC complex solution show largest values at mass concentration ratio of 1.5, which is near the maximum binding of HTAC to PEO in dilute aqueous solution. It was confirmed that the progressive increase on the PEO-HTAC aggregates induced a cross-linking between PEO and HTAC, leading to an increase in the modulus.

Finally, the interaction between nonionic polymer, hydroxypropyl cellulose (HPC), and amphoteric surfactant, cocamidopropyl dimethyl glycine (CADG), was studied by means of viscosity and light scattering measurements in an isoelectric point (pH = 9). The viscosity and dynamic light scattering showed that a maximum and a minimum occurred [HTAC]/[PEO] ratios (c_s/c_p) at 0.026 and 0.43. From Zimm plot analysis, the molecular weight of complex ($M_{w,com}$)was approximately equal to the molecular weight of pure HPC at maximum point, indicating that there was no interaction between HPC and CADG at $c_s/c_p = 0.026$. The increases in $M_{w,com}$ and the number of bound CADG to HPC were observed due to the binding between polymer and surfactant. At the binding condition, the minimum value was observed because of the electrostatic attractions between positive and negative charges within the polymer chain.

บทคัดย่อ

คายน์ ยี เมี้ย : สมบัติทางกายภาพและสภาพการไหลของสารประกอบร่วมของพอลิเมอร์ชนิดไร้ประจุและสารลดแรงตึงผิวประเภทมีประจุ (Physical and Rheological Properties of Nonionic Polymers – Ionic Surfactants Complexes) อ.ที่ปรึกษา : ศ.ดร. อเล็กซานเดอร์ เอ็ม เจมีสัน และ รศ.ดร. อนุวัฒน์ ศิริวัฒน์ 376 หน้า ISBN 974-03-1553-4

การก่อตัวของสารประกอบร่วมพอลิเมอร์และสารลดแรงตึงผิว โดยการรวมกันระหว่างพอลิเมอร์ประเภทไร้ประจุ พอลิเอธิลีนออกไซด์ (PEO) กับสารลดแรงตึงผิวประเภทประจุบวก เฮกซะเดคซิลไตรเมธิลแอมโมเนียมคลอไรด์ (HTAC) ได้มีการศึกษาโดยการสังเกตการเปลี่ยนแปลง ค่าการนำไฟฟ้า ค่าความหนืดจำเพาะ (η_{sp}) และค่ารัศมีไฮโดรไดนามิก (R_h) ข้อมูลการนำไฟฟ้าแสดงให้เห็นว่าการทำปฏิกิริยาต่อกันระหว่าง PEO และ HTAC เกิดขึ้นที่อุณหภูมิสูงกว่า 25 องศาเซลเซียสขึ้นไป ซึ่งเห็นได้จากการลดลงของค่าความเข้มข้นวิกฤติของการรวมตัวในระบบที่มี PEO เทียบกับค่าความเข้มข้นวิกฤตของการเกิดไมเซลล์ของสารลดแรงตึงผิว ในระบบที่ไม่มี PEO การรวมตัวกันของ HTAC และ PEO ทำให้สายของพอลิเมอร์ขยาย เนื่องจากแรงผลักทางไฟฟ้าสถิตย์ระหว่างพันธะในไมเซลล์ เมื่อเพิ่มปริมาณของ HTAC ค่า η_{sp} และ R_h จะขึ้นไปสู่ค่าสูงสุดที่สภาวะอิ่มในการรวมตัว หลังจากนั้นจะลดลง เนื่องจากการหดตัวของาสารประกอบร่วม PEO และ HTAC ซึ่งเกิดจากการบดบังทางไฟฟ้าสถิตย์จากการรวมตัวกันของไมเซลล์อิสระ และประจุไฟฟ้าตรงข้ามในสารละลาย

จากการศึกษาด้านกระเจิงแสงสถิตย์ โครงสร้างของสารประกอบร่วม PEO-HTAC ได้มีการศึกษาในเรื่องของ การวัดขนาดมวลโมเลกุล ที่อัตราส่วนความเข้มข้นของ HTAC ต่อ PEO ที่แตกต่างกัน การเกิดสารประกอบร่วมแบบหลายโซ่พบได้ในสารละลายที่มีน้ำเป็นตัวทำละลาย ในสภาวะที่เกิดการรวมตัวสูงสุด อย่างไรก็ตาม ภายหลังจากการเติม KNO_3 1 โมล โครงสร้างของสารประกอบร่วมมีการเปลี่ยนแปลงจากรูปร่างหลายโซ่ไปเป็นสารประกอบร่วมสายโซ่เดี่ยว ยิ่งไปกว่านั้น จำนวนของพันธะระหว่างโมเลกุล HTAC ต่อ PEO มีค่าเพิ่มขึ้นจาก 0.12 โมล HTAC ต่อ 1 โมล PEO ไปเป็น 0.23 โมล HTAC ต่อ 1 โมล PEO ในสารละลายเกลือ

การวัดค่าสภาพการไหลยังแสดงให้เห็นว่า ค่ามอดูลัสความเป็นของแข็ง (G') และค่ามอดูลัสความเป็นของเหลว (G") ของสารละลายเข้มข้น PEO-HTAC มีค่าสูงสุดเมื่ออัตราส่วนความเข้มข้น

โดยมวลเป็น 1.5 ซึ่งใกล้เคียงกับค่าสูงสุดในการรวมตัวกันของ HTAC และ PEO ในสารละลายเจือจาง การทดลองนี้ได้รับการยืนยันว่า การเพิ่มขึ้นของการรวมตัวกันระหว่าง PEO และ HTAC ทำให้เกิดพันธะร่วมกันระหว่าง PEO และ HTAC และนำมาสู่การเพิ่มขึ้นของค่ามอดูลัส

ปฏิกิริยาสัมพันธ์กันระหว่างพอลิเมอร์ไร้ประจุ ไฮดรอกซีโพรพิลเซลลูโลส (HPC) และสารลดแรงตึงผิวประเภทประจุคู่ โคคามิโดรโพรพิลไดเมธิลไกลซีน (CADG) ได้รับการศึกษาจากค่าความหนืดและจากการวัดค่าการกระเจิงแสงที่จุดไอโซอิเล็กทรก (pH=9) ค่าความหนืด และค่าการกระเจิงแสงไดนามิก แสดงให้เห็นว่า ค่ามากที่สุด และค่าน้อยที่สุด จะเกิดขึ้นเมื่ออัตราส่วนของ HTAC ต่อ PEO อยู่ที่ 0.026 และ 0.43 จากากรวิเคราะห์โดยซิมพลอต ค่ามวลโมเลกุลของสารประกอบร่วม ($M_{w,com}$) จะมีค่าโดยประมาณเทียบเท่ากับค่า มวลโมเลกุลของ HPC ที่จุดสูงสุด ซึ่งแสดงให้เห็นว่าไม่มีปฏิกิริยาสัมพันธ์กันระหว่าง HPC และ CADG ที่อัตราส่วน HTAC ต่อ PEO เท่ากับ 0.026 การเพิ่มขึ้นของค่ามวลโมเลกุลของสารประกอบร่วม และจำนวนพันธะระหว่าง CADG กับ HPC พบว่าเกิดจากการรวมตัวกันระหว่างพอลิเมอร์ และสารลดแรงตึงผิว ที่สภาวะที่มีการรวมตัวต่ำสุด พบว่าเกิดจากการดึงดูดกันทางไฟฟ้าสถิตย์ระหว่างประจุบวกและลบภายในสายพอลิเมอร์

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and appreciation to the Petroleum and Petrochemical College (PPC) for providing the scholarship for my doctoral program and special thanks to National Metals and Materials Technology Center (MTEC) for funding the research work.

I express my deepest appreciation to my advisor, Professor Alexander M. Jamieson of Case Western Reserve University, Cleveland, Ohio, USA, for providing valuable suggestions, inspiring guidance, and giving me the opportunity to do my research work in his lab for 3 months.

My sincere gratitude to my advisor, Associate Prof. Anuvat Sirivat, for his continuous advice, motivation and support for the success of this study, and providing me with the chance to present my research work in Thailand and USA.

I would like to extend my heartfelt thanks to Associate Professor Kunchana Bunyakiat, Assistant Prof. Nantaya Yanumet, and Dr. Asira Fuongfuchat, who acted as committee members.

I also extend my sincere thanks to all of the staff of the Petroleum and Petrochemical College for giving the permission to freely use the research facilities.

Most of all, this work is dedicated to my parents and my husband, for their tender love and care, generous encouragement, understanding and moral support during this study.

TABLE OF CONTENTS

		PAGE
	Title Page	i
	Abstract (in English)	iii
	Abstract (in Thai)	v
	Acknowledgements	vii
	Table of Contents	viii
	List of Tables	xv
	List of Figures	xvii
	Abbreviations	xxiv
	List of Symbols	xxv
CHAPTER		
I	**INTRODUCTION**	1
	1.1 Types of Polymer-Surfactant Complexes	1
	1.1.1 Uncharged Polymer with Anionic Surfactant	1
	1.1.2 Uncharged Polymer with Cationic Surfactant	2
	1.1.3 Uncharged Polymer with Nonionic Surfactant	2
	1.1.4 Polyelectrolyte with Oppositely Charged Surfactant	3
	1.2 Structures of Polymer-Surfactant Complexes	3
	1.3 General Aspects of Interactions	5
	1.3.1 Binding Isotherms	6
	1.3.2 Strength of Interaction	7
	1.4 Technical Applications of Polymer-Surfactant Complexes	8
	1.4.1 Rheology Control	8
	1.4.2 Pharmaceutical Applications	9
	1.4.3 Cosmetic Formulation	10

CHAPTER **PAGE**

1.4.4 Solubilization 10

1.4.5 Detergency 10

1.4.5.1 Increasing Soil Removal 10

1.4.5.2 Dye Transfer Inhibition 10

1.4.5.3 Preventing Particulate Soil Redeposition 11

1.5 Rheology 11

1.5.1 Viscoelastic Properties of Polymeric Materials 11

1.5.2 Viscoelastic Properties of Surfactant Solutions 12

1.6 Polymers 14

1.6.1 Poly(Ethylene Oxide) (PEO) 14

1.6.2 Hydroxypropyl Cellulose (HPC) 15

1.7 Surfactant Solutions 15

1.7.1 Hexadecyltrimethylammonium Chloride (HTAC) 15

1.7.2 Cocamidopropyl Dimethyl Glycine (CADG) 16

1.8 Objectives 16

II LITERATURE SURVEY 18

2.1 Interactions of Polymer-Surfactant Complexes in Dilute Solutions 18

2.1.1 Nonionic Polymer-Anionic Surfactant 18

2.1.2 Nonionic Polymer-Cationic Surfactant 20

2.1.3 Nonionic Polymer-Nonionic Surfactant 22

2.1.4 Polyelectrolyte-Oppositely Charged Surfactant 24

2.2 Rheological Investigations on Polymer-Surfactant Complexes 26

CHAPTER **PAGE**

2.3 Summary 28

2.4 Rheological Studies on Flexible Elongated Micelles 32

III EXPERIMENTAL 36

3.1 Materials 36

3.2 Apparatus 37

3.2.1 Capillary Viscometer 37

3.2.1.1 Cannn-Ubbelohde Viscometer 37

3.2.1.2 Thermostatic Water Bath 37

3.2.1.3 Timing Device 37

3.2.2 Filtering Accessories 37

3.2.3 Centrifuge 37

3.2.4 Conductivity Meter 38

3.2.5 Du-Nouy Ring Tensiometer 38

3.2.6 pH Meter 38

3.2.7 Dialysis Membrane 38

3.2.8 Refractometer 38

3.2.9 Light Scattering Instrument 38

3.2.10 Rheometer 39

3.3 Sample Preparation 39

3.3.1 Preparation of Polymer Solutions 39

3.3.2 Preparation of Surfactant Solutions 40

3.3.3 Preparation of Polymer-Surfactant Complex Solutions 40

3.4 Methodology 41

3.4.1 Measurements of cmc and cac 41

CHAPTER **PAGE**

3.4.2 Viscosity Measurement 42

3.4.3 Dialysis Experiment 44

3.4.4 Refractive Index Measurement 46

3.4.5 Light Scattering Measurements 47

3.4.5.1 Static Light Scattering 48

3.4.5.2 Dynamic Light Scattering 53

3.4.6 Rheological Measurements 57

3.4.6.1 Rheological Measurements 57

3.4.6.2 Viscoelastic Properties of Surfactant Solutions 61

IV RESULTS AND DISCUSSION 62

4.1 Binary System of PEO-Water Mixture 62

4.1.1 Molecular Weight Measurement 62

4.1.1.1 Viscosity 62

4.1.1.2 Light Scattering 63

4.1.2 Measurement of Hydrodynamic Radius (R_h) 64

4.1.3 dn/dc Measurement 66

4.2 Binary System of HTAC Solution 67

4.2.1 Determination of Critical Micelle Concentration (cmc) 67

4.2.1.1 Surface Tension 67

4.2.1.2 Conductivity 68

4.2.2 Viscosity Measurement 70

4.3 Ternary System of PEO/HTAC/Water 71

4.3.1 Effect of Surfactant Concentration 71

4.3.1.1 Conductivity Measurement 71

CHAPTER **PAGE**

4.3.1.2 Viscosity and R_h Measurement 72

4.3.2 Effect of Polymer Concentration 74

4.3.2.1 Viscosity Measurement 74

4.3.2.2 R_h Measurement 76

4.3.3 Effect of Temperature 78

4.3.3.1 Measurements of cmc and cac 78

4.3.3.2 Viscosity Measurement 79

4.3.3.3 Hydrodynamic Radius (R_h) Measurement 82

4.3.4 Effect of Molecular Weight 83

4.3.4.1 Viscosity Measurement 83

4.3.4.2 Measurement of R_h 85

4.3.5 Effect of Salt 86

4.3.5.1 Conductivity Measurement 86

4.3.5.2 Viscosity Measurement 87

4.3.6 Determination of the Structure of PEO-HTAC Complex 88

4.3.6.1 PEO-HTAC Complex in Water 88

4.3.6.2 PEO-HTAC Complex in 0.1 M KNO_3 Solution 97

4.4 Viscoelastic Properties of PEO in Water 103

4.4.1 Salt Effect 104

4.4.2 Temperature Effect 105

4.5 Viscoelastic Properties of HTAC Micelles 108

4.6 Viscoelastic Properties of PEO-HTAC Complex Solutions 116

4.6.1 PEO-HTAC Complex in Water 116

CHAPTER		PAGE
	4.6.2 PEO-HTAC Complex in 0.1 M KNO_3 Solution	123
	4.7 Investigation of HPC-CADG Interaction	125
	4.7.1 cmc and cac Measurements	125
	4.7.2 Viscosity Measurement	127
	4.7.3 Hydrodynamic Radius Measurement	128
	4.7.4 Determination of Structure of HPC-CADG System	129
V	**CONCLUSIONS AND RECOMMENDATIONS**	132
	5.1 Interaction of PEO-HTAC Complex in Dilute Solutions	132
	5.1.1 Effect of Surfactant Concentration	132
	5.1.2 Effect of Polymer Concentration	132
	5.1.3 Effect of Temperature	132
	5.1.4 Effect of Molecular Weight	133
	5.1.5 Effect of Salt	133
	5.2 The Structures of PEO-HTAC Complex in Dilute Solutions	133
	5.2.1 Effect of Ionic Strength	134
	5.3 Viscoelastic Properties of PEO in Water	135
	5.4 Viscoelastic Properties of HTAC Micelles	135
	5.5 Viscoelastic Properties of PEO-HTAC Complexes	136
	5.6 Interaction of HPC-CADG Complex in Dilute Solutions	137
	5.7 Recommendations	138

CHAPTER		PAGE
	REFERENCES	139
	APPENDICES	149
	APPENDIX - 1	149
	APPENDIX - 2	164
	APPENDIX - 3	167
	APPENDIX - 4	241
	APPENDIX - 5	265
	APPENDIX - 6	272
	APPENDIX - 7	357
	CURRICULUM VITAE	373

LIST OF TABLES

TABLE		PAGE
1.1	The cmc values for surfactant micelles in water and the corresponding cac values in the presence of polymer	9
2.1	Literature studies of the interactions between polymers and surfactants	28
2.2	Previous studies of physical parameters determination by static light scattering measurement	30
2.3	Investigation of physical parameters by static light scattering measurement	32
2.4	Summary for the rheological studies of elongated worm-like micelles	35
4.1	Zimm plot results for PEO in water at 30°C	64
4.2	Viscosity and light scattering results for PEO in aqueous solution	66
4.3	The saturation concentrations of HTAC and the saturation ratios of HTAC/PEO at different PEO concentrations	76
4.4	Refractive index increments and molecular weight obtained by thermodynamic treatment method	91
4.5	Physical parameters of PEO(2)-HTAC complexes obtained from light scattering measurements	92
4.6	Variation of $M_{w,com}$, R_g, $R_{h,f}$, and $R_{h,\eta}$ with addition of HTAC	93
4.7	The comparative study of PEO-HTAC complex in aqueous solution and in the presence of 0.1 M KNO_3 solution at the maximum binding point	99
4.8	The deviation from single exponential function, together with the values of G_0 and η_0 at different temperatures	114
4.9	The data of DFS, $\bar{\zeta}$, τ_R and τ_b for different temperatures	115

TABLE **PAGE**

4.10	Physical parameters of HPC-CADG complexes at different c_s/c_p ratios, determined by refractive index and light scattering measurements	131
5.1	Summary for the formation of PEO-HTAC complex	137

LIST OF FIGURES

FIGURE		PAGE
1.1	Schematic representations of structures of polymer-surfactant complexes	4
1.2	A typical isotherm for the binding of a surfactant to a polymer	6
1.3	Symbolic representation of long-range and short-range contour relationships in a flexible polymer molecules	11
1.4	Schematic representation of a Cole-Cole plot	14
1.5	Chemical structure of hydroxypropylcellulose (HPC)	15
1.6	Chemical structure of hexadecyltrimethylammonium chloride (HTAC)	16
1.7	Chemical structure of cocamidopropyl dimethyl glycine (CADG): (a) in solid form, (b) in aqueous solution	16
3.1	Flow chart diagram for dilute polymer-surfactant solution preparation	40
3.2	Diagram for concentrated polymer-surfactant solution preparation	41
3.3	Effect of micelle formation on surface tension of a surfactant solution	42
3.4	Schematic diagram for the determination of critical micelle concentration (cmc) and critical aggregation concentration (cac)	42
3.5	Schematic diagram of simple dialysis experiment	45
3.6	Diagram describing the bending of light rays by refractive index gradient	46
3.7	The schematic diagram of light scattering instrument	49
3.8	The general features of time intensity autocorrelation function	54

FIGURE **PAGE**

3.9	Linear viscoelastic spectrum of the shear storage modulus, G' and loss modulus, G" for an entangled polymer solution	58
3.10	Schematic of cone and plate geometry utilized in fluid rheometry	61
4.1	Reduced viscosity (η_{red}/c_p) as a function of PEO concentration for PEO(2) solution at 30°C	63
4.2	Zimm plot for PEO(2) solution in water at 30°C	64
4.3	Apparent diffusion coefficient (D_{app}) as a function of square of scattering wave vector (q^2) at different PEO concentrations	65
4.4	Center of mass diffusion coefficient vs. PEO concentration	66
4.5	Refractive index of PEO as a function of PEO concentration	67
4.6	Surface tension of HTAC in water as a function of HTAC concentration at 30°C	68
4.7	Variation of conductivity with HTAC concentration to determine the critical micelle concentration (cmc)	69
4.8	Variation of the conductivity of HTAC solution with the HTAC concentration at 30°C in the presence of 0.1 M KNO_3	69
4.9	Semi-logarithmic plot of the specific viscosity as a function of HTAC concentration	70
4.10	Variation of conductivity with HTAC concentration in the presence of PEO(2)	71
4.11	Specific viscosity (η_{sp}) as a function of HTAC concentration for PEO(2) solutions	72
4.12	Center of mass diffusion coefficient (D_{cm}) as a function of HTAC concentration for PEO(2) solution	73
4.13	Dependence of specific viscosity on surfactant concentration at different polymer concentrations	74
4.14	Dependence of specific viscosity on c_s/c_p ratio at different PEO concentrations	75

FIGURE **PAGE**

4.15	Diffusion coefficient as a function of surfactant to polymer concentration ratio (c_s/c_p)	77
4.16	Hydrodynamic radius (R_h) as a function of surfactant to polymer concentration ratio (c_s/c_p)	77
4.17	Variation of the cmc and the cac with temperature for HTAC in water and in the presence of PEO	78
4.18	Dependence of specific viscosity on HTAC concentration at four different temperatures	79
4.19	Temperature dependence of specific viscosity on surfactant concentration	81
4.20	Apparent hydrodynamic radius (R_h) as a function of HTAC concentration at three different temperatures	82
4.21	Dependence of specific viscosity on HTAC concentration at four different PEO molecular weights	83
4.22	The ratio of η_{sp}(PEO+HTAC)/η_{sp}(PEO) as a function of HTAC concentration	84
4.23	Dependence of apparent hydrodynamic radius on HTAC concentration at different PEO molecular weights	85
4.24	Variation of the conductivity of PEO-HTAC complex with HTAC concentration at 30°C in the presence of 0.1 M KNO_3	86
4.25	Dependence of specific viscosity on HTAC to PEO concentration ratio in water (O); and in the presence of 0.1 M KNO_3 solution (□). PEO concentration: 0.1 g/dL.	87
4.26	Zimm plot for PEO(2)-HTAC complex solution at the maximum binding point (c_s/c_p = 1.75)	89
4.27	Molecular weight of PEO(2)-HTAC complex as a function of surfactant to polymer concentration ratio in ternary solution at 30°C	94

FIGURE **PAGE**

4.28	Radius of gyration and apparent hydrodynamic radius as a function of HTAC to PEO concentration ratio for PEO(2)-HTAC complex	94
4.29	Zimm plot for PEO-HTAC complex solution in 0.1 M KNO_3 solution at 30°C, at the maximum binding point (c_s/c_p = 1.75)	98
4.30	The particle size distribution of PEO solution	102
4.31	The particle size distribution of PEO-HTAC solution at HTAC/PEO ratio = 1.75 (maximum binding point)	102
4.32	Double logarithmic plot of the storage modulus (G'), the loss modulus (G"), and the complex viscosity (η^*) as a function of frequency (ω) for PEO 4 g/dL at 30°C	103
4.33	Double logarithmic plot of the storage modulus G', the loss modulus G", and the complex viscosity η^* as a function of frequency ω for PEO 8 g/dL at 30°C	104
4.34	Double logarithmic plot of G', G", and η^* as a function of ω for 4 g/dL PEO in water (open, closed, and dotted circles) and in 0.1 M KNO_3 solution (open, closed, and dotted squares) at 30°C	104
4.35	Double logarithmic plot of the reduced storage modulus G_R', and the reduced loss modulus G_R" versus the reduced frequency ω_R for PEO 4 g/dL at different temperatures	105
4.36	Double logarithmic plot of the reduced storage modulus G_R', and the reduced modulus G_R" versus the reduced frequency ω_R for PEO 8 g/dL at different temperatures	106
4.37	The complex viscosity η^* versus frequency for PEO 4 g/dL at different temperatures	107
4.38	The complex viscosity η^* versus frequency for PEO 8 g/dL at different temperatures	107

FIGURE **PAGE**

4.39	The complex viscosity (η^*) as a function of frequency for two different concentrations	108
4.40	The schematic drawing for flexible wormy micelles	109
4.41	Logarithmic plot of the storage modulus G', the loss modulus G" versus frequency for a solution of 0.5 M HTAC (16 g/dL) at different temperatures	110
4.42	The temperature dependence of plateau modulus (G_0) and the stress relaxation time (τ_R)	111
4.43	The variation of the complex viscosity (η^*) as a function of frequency at different temperatures for 0.5 M HTAC (16 g/dL) solution	111
4.44	The Cole-Cole plot, represented as the loss modulus G" versus the storage modulus G', for 0.5 M HTAC solution at different temperatures	113
4.45	Experimental Cole-Cole diagram, plotted as $\mu"(\omega)$ vertical and $\mu'(\omega)$ horizontal) for five different	114
4.46	Diameter of fitted semicircle (DFS) plotted against $\bar{\zeta}$ (horizontal axis). Numerical points joined by simple interpolation and constrained to pass through (1,0)	115
4.47	The reduced moduli (G_R' and $G_R"$) as a function of reduced frequency (ω_R) for PEO (4 g/dL)-HTAC (2 g/dL) ($c_s/c_p = 0.5$) at different temperatures	116
4.48	The complex viscosity as a function of frequency for PEO-HTAC at $c_s/c_p = 0.5$ at different temperatures	117
4.49	The reduced moduli (G_R' and $G_R"$) as a function of reduced frequency (ω_R) for PEO (4 g/dL)-HTAC (6 g/dL) ($c_s/c_p = 1.5$) at different temperatures	118
4.50	Frequency dependence of viscosity at different temperatures for $c_s/c_p = 1.5$	118

FIGURE **PAGE**

4.51	Master curve for PEO (4 g/dL)-HTAC (8 g/dL) at c_s/c_p = 2.0 at different temperatures	119
4.52	The complex viscosity versus frequency for c_s/c_p = 2.0 at different temperatures	120
4.53	The complex viscosity as a function of temperature for different HTAC concentration	121
4.54	The reduced storage and loss moduli (G_R' and G_R") as a function of reduced frequency (ω_R) for PEO-HTAC complex at c_s/c_p = 1.5	121
4.55	The logarithmic plot of complex viscosity as a function of frequency at different temperatures	122
4.56	The temperature dependence of complex viscosity for different HTAC concentrations	123
4.57	The reduced storage (G_R') and loss moduli (G_R") plotted as a function of reduced frequency (ω_R) for PEO (4 g/dL) and HTAC (6 g/dL) in 0.1 M KNO_3 solution at c_s/c_p = 1.5 at different temperatures	124
4.58	The frequency dependence of complex viscosity for PEO (4 g/dL)-HTAC (6 g/dL) in 0.1 M KNO_3 solution at c_s/c_p = 1.5 for five different temperatures	124
4.59	Dependence of critical micelle concentration (cmc) on pH at 30°C for amphoteric surfactant (CADG) solutions	126
4.60	The variation of conductivity of CADG in the presence of HPC as a function of CADG concentration at pH = 9	127
4.61	The specific viscosity (η_{sp}) as a function of CADG concentration at 30°C for HPC-CADG system at pH = 9	128
4.62	The apparent hydrodynamic radius (R_h) of HPC as a function of CADG concentration at pH = 9 for HPC-CADG system	128

FIGURE **PAGE**

4.63	Zimm plot for HPC-CADG system at $c_s/c_p = 0.026$	130
4.64	Zimm plot for HPC-CADG system at $c_s/c_p = 0.43$	130
5.1	The proposed model for PEO-HTAC complex in aqueous solution at maximum binding	134
5.2	The proposed model for PEO-HTAC complex in 0.1 M KNO_3 solution at maximum binding	135

ABBREVIATIONS

Polymers:

PEO	Poly(ethylene oxide)
EHEC	Ethylhydroxyethyl cellulose
PVP	Poly(vinyl pyrrolidone)
PVME	Poly(vinylmethyl ether)
POE	Poly(oxyethylene)
PEG	Poly(ethylene glycol)
HPC	Hydroxypropyl cellulose
HEC	Hydroxyethyl cellulose
PPO	Poly(propylene oxide)
PAM	Polyacrylamide
PVPNO	Poly(4-vinylpyridine N-oxide)
PCMA	Poly(N,N,N-trimethylammonio) ethyl acrylate
PAA	Polyacrylic acid
PE	Polyelectrolytes

Surfactants:

SDS	Sodium dodecylsulfate
DDAB	Didodecyldimethylammonium bromide
HTAB, HTAC	Hexadecyltrimethylammonium bromide and chloride
DoTAB	Dodecyltrimethylammonium bromide
HTASal	Hexadecyltrimethylammonium salicylate
CTAB, CTAC	Cetyltrimethylammonium bromide and chloride
TTAB	Tetradecyltrimethylammonium bromide
RTAB, RTAC	Alkyltrimethylammonium bromide and chloride
NP_{14}, NP_{20}	Polyethylene oxide nonyl phenyl ether
Slovafol 909	Nonylphenol polyethylene glycol
OTG	N-octyl thioglucoside
$C_{12}E_5$	Pentaethylene glycol mono-n-dodecyl ether

LIST OF SYMBOLS

cmc = Critical micelle concentration

cac = Critical aggregation concentration

M_w = Molecular weight of polymer in binary system

$M_{w,p}$ = Molecular weight of polymer in the complex

$M_{w,com}$ = Molecular weight of complex

D' = Preferential binding of surfactant to polymer

f = Binding fraction

N_s/N_p = Total number of surfactant per polymer chain

$N_{s,b}/N_p$ = Number of bound surfactant per polymer chain

R_g = Radius of gyration

R_h = Hydrodynamic radius

η_{sp} = Specific viscosity

η^* = Complex viscosity

η_0 = Zero-shear viscosity

G_0 = Shear plateau modulus

G'= Shear storage modulus

G" = Shear loss modulus

G_R' = Reduced storage modulus

G_R" = Reduced loss modulus

ω_R = Reduced frequency

τ_R = Terminal relaxation time

τ_{break} = Breaking time of worm-like micelle

τ_{rep} = Reptation time of worm-like micelle