

**TURBULENT WALL SHEAR STRESS MEASUREMENT IN AQUEOUS
SOLUTIONS CONTAINING POLY(ETHYLENE OXIDE) AND
HEXADECYLTRIMETHYLAMMONIUM CHLORIDE COMPLEXES**

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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

2006

ISBN 974-9990-11-0

492217

Thesis Title: Turbulent Wall Shear Stress Measurement in Aqueous Solutions Containing Poly(ethylene oxide) and Hexadecyltrimethylammonium Chloride Complexes

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Program: Petrochemical Technology

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ABSTRACT

4391004063: Petrochemical Technology Program

Siriluck Suksamranchit: Turbulent Wall Shear Stress Measurement in Aqueous Solutions Containing Poly(ethylene oxide) and Hexadecyltrimethylammonium Chloride Complexes.

Thesis Advisors: Assoc. Prof. Anuvat Sirivat and Prof. Alexander M. Jamieson 247 pp. ISBN 974-9990-11-0

Keywords: Turbulent wall shear stress/ Poly(ethylene oxide)/ Cationic surfactant/Hexadecyltrimethylammonium Chloride/Couette flow

Turbulent drag reduction in Couette flow was investigated in term of wall shear stress measurement for aqueous solutions of a nonionic polymer, poly(ethylene oxide) (PEO), a cationic surfactant, hexadecyltrimethylammonium chloride (HTAC), and their complexes. Drag reduction can be observed for PEO solutions above a critical molecular weight, $0.91 \times 10^5 < M_c < 3.04 \times 10^5$. Minimum wall shear stress occurs at an optimum concentration, c_{PEO}^* , which scales inversely with molecular weight, and the %maximum drag reduction increases with molecular weight. For aqueous HTAC solutions, wall shear stress decreases with increasing HTAC concentration and levels off at an optimum concentration, c_{HTAC}^* , comparable to the critical micelle concentration. For PEO-HTAC mixtures, the critical PEO molecular weight for drag reduction decreases, interpreted as due to an increase in hydrodynamic volume because of binding of HTAC micelles to PEO. Consistent with this interpretation, at fixed PEO concentration, minimum wall shear stress is observed at an optimum HTAC concentration, $c_{HTAC/PEO}^*$, comparable to the maximum binding concentration, MBC. For the aqueous PEO-HTAC in salt solutions, addition of salt reduces the hydrodynamic radius of PEO-HTAC complex. These observations are consistent with the scenarios of the polymer chain contraction via electrostatic screening and the dissociation of multichain complexes. The minimum wall shear stress measurement of the aqueous HTAC solution occurs at the optimum HTAC concentration; its value decreases with increasing ionic strength. For

the aqueous PEO-HTAC solution titrated with HTAC, wall shear stresses upon addition of HTAC beyond the respective CMC values are strongly reduced as ionic strength increases. For the aqueous PEO-HTAC solution titrated with PEO, minimum wall shear stress occurs at an optimum PEO concentration, which is smaller than that of pure PEO, and whose value increases with ionic strength.

บทคัดย่อ

สิริลักษณ์ สุขสำราญจิตต์ : การวัดค่าความเครียดเฉือนที่ผนังในการไหลแบบปั่นป่วน ซึ่งเกิดขึ้นในสารละลายน้ำที่ประกอบด้วยพอลิเอทิลีนออกไซด์และเฮกซะเดซิลไตรเมทิลแอมโมเนียมคลอไรด์ (Turbulent Wall Shear Stress Measurement in Aqueous Solutions Containing Poly(ethylene oxide) and Hexadecyltrimethylammonium Chloride Complexes.) อ. ที่ปรึกษา : รศ.ดร. อนุวัฒน์ ศิริวัฒน์ และ ศ.ดร. อเล็กซานเดอร์ เอ็ม เจมิชอัน 247 หน้า ISBN 974-9990-11-0

การลดแรงเสียดทานในการไหลแบบปั่นป่วนภายในเซลล์ทรงกระบอกรูปวงแหวน ได้รับการศึกษาโดยการวัดค่าความเครียดเฉือนที่ผนังของสารละลายน้ำที่ประกอบด้วยพอลิเมอร์ประเภทไร้ประจุ พอลิเอทิลีนออกไซด์ (พีอีโอ) และสารลดแรงตึงผิวประเภทประจุบวกเฮกซะเดซิลไตรเมทิลแอมโมเนียมคลอไรด์ (เอชทีเอซี) และสารประกอบร่วมของมัน ในสารละลายพีอีโอ พบว่าการลดแรงเสียดทานเกิดขึ้นเมื่อน้ำหนักโมเลกุลของพีอีโอสูงกว่าน้ำหนักโมเลกุลวิกฤติ โดย $0.91 \times 10^5 < \text{น้ำหนักโมเลกุลวิกฤติ} < 3.04 \times 10^5$ กรัมต่อโมล ค่าความเครียดเฉือนที่ผนังที่ต่ำที่สุดเกิดขึ้นที่ค่าความเข้มข้นออสโมติก c^*_{PEO} ซึ่งค่านี้แปรผกผันกับน้ำหนักโมเลกุลของพีอีโอ และค่าเปอร์เซ็นต์ของการลดแรงเสียดทานเพิ่มขึ้นเมื่อน้ำหนักโมเลกุลของพีอีโอเพิ่มขึ้น สำหรับสารละลายเอชทีเอซี ค่าความเครียดเฉือนที่ผนังลดลงเมื่อความเข้มข้นเอชทีเอซีเพิ่มขึ้นและคงที่เมื่อความเข้มข้นเอชทีเอซีอยู่ที่ค่าความเข้มข้นออสโมติก c^*_{HTAC} ซึ่งค่านี้ใกล้เคียงกับค่าความเข้มข้นวิกฤติในการเกิดไมเซลล์ (ซีเอ็มซี) สำหรับสารละลายผสมพีอีโอ – เอชทีเอซี ค่าน้ำหนักโมเลกุลวิกฤติของพีอีโอในการลดแรงเสียดทานลดลงเพราะปริมาตรไฮโดรไดนามิกที่เพิ่มขึ้นเนื่องจากการรวมกันระหว่างไมเซลล์ของเอชทีเอซีบนพีอีโอซึ่งสอดคล้องกับการสังเกตที่ว่าเมื่อให้ค่าความเข้มข้นของพีอีโอคงที่ ค่าความเครียดเฉือนที่ผนังที่ต่ำสุดเกิดขึ้นที่ความเข้มข้นออสโมติกเอชทีเอซี $c^*_{HTAC/PEO}$ โดยค่านี้ใกล้เคียงกับค่าความเข้มข้นเอ็มบีซี ซึ่งเป็นค่าความเข้มข้นเอชทีเอซีสูงสุดในการรวมตัวกันระหว่างเอชทีเอซีกับพีอีโอ สำหรับสารผสมพีอีโอ – เอชทีเอซีในสารละลายเกลือ พบว่าการเติมเกลือลงไปจะลดค่ารัศมีไฮโดรไดนามิกของสารผสมพีอีโอ – เอชทีเอซี ข้อสังเกตนี้สอดคล้องกับการที่พบว่าสายโซ่ของพอลิเมอร์มีการหดตัวเนื่องจากอิทธิพลของประจุทางไฟฟ้าและการแตกตัวของสายโซ่ในสารละลายผสมพีอีโอ – เอชทีเอซี ค่าความเครียดเฉือนที่ผนังที่ต่ำสุดของสารละลายเอชทีเอซีเกิดขึ้นที่ความเข้มข้นออสโมติกเอชทีเอซี โดยค่านี้ลดลงเมื่อความเข้มข้นของประจุมากขึ้น สำหรับสารละลายผสมพีอีโอ – เอชทีเอซีเมื่อใดก็ตามที่ปริมาณเอชทีเอซีที่เพิ่มขึ้น พบว่าค่าความเครียดเฉือนที่ผนังเมื่อเติมเอชทีเอซีมากกว่าค่าซีเอ็มซีของสารผสมนั้นจะ

ลงอย่างมากเมื่อความเข้มข้นของประจุเพิ่มมากขึ้น ในขณะที่สารละลายผสมพีอีโอ – เอชทีเอชเมื่อใดตรงกับปริมาณพีอีโอที่เพิ่มขึ้น พบว่าความเข้มข้นออกซิเจนพีอีโอซึ่งเกิดขึ้นในสารละลายผสมพีอีโอ – เอชทีเอช มีค่าต่ำกว่าค่าความเข้มข้นออกซิเจนพีอีโอในสารละลายพีอีโอ และค่านี้เพิ่มขึ้นเมื่อความเข้มข้นของประจุเพิ่มขึ้น

ACKNOWLEDGEMENTS

This research 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 acknowledge the financial support from the Thailand Research Fund (TRF), the Royal Golden Jubilee (RGJ), grant no. PHD/0149/2543. This work was financially supported by the fund from MTEC, grant no. MT-43-POL-09-144-G, the fund from the ADB Consortium Grant and the fund from Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

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, her advisor for his valuable suggestions, motivation, constructive criticism and proof-reading of manuscripts and this dissertation book. The author express her deepest appreciation to her advisor, Professor Alexander M. Jamieson of Case Western Reserve University, Cleveland, Ohio, USA, for providing valuable suggestions, inspiring guidance, and giving her the opportunity to do her research work in his lab for 3 months. The author appreciates Assistant Professor Pitt Supaphol and Dr. Nispa Seetapan for being research committee members.

The author would like to give special thanks to the Unilever Thai Holding Co., Ltd. for raw materials support.

The author thanks all of her friends who encouraged her in carrying out the experiment and moral support. The author also extends her sincere thanks to all of the staffs of the Petroleum and Petrochemical College for giving the permission to freely use the research facilities.

Most of all, the author would like to dedicate this work to her parents and family, for their tender love and care, generous encouragement, understanding, financial 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	xii
List of Figures	xiv
Abbreviations	xxii
List of Symbols	xxiii
 CHAPTER	
I INTRODUCTION	1
 II LITERATURE SURVEY	 4
 III EXPERIMENTAL	 15
 IV POLYMER-SURFACTANT COMPLEX FORMATION AND ITS EFFECT ON TURBULENT WALL SHEAR STRESS	 20
4.1 Abstract	20
4.2 Introduction	20
4.3 Experimental	22
4.4 Results and Discussion	27
4.5 Conclusions	35
4.6 Acknowledgements	36
4.7 References	36

CHAPTER	PAGE
V INFLUENCE OF IONIC STRENGTH ON COMPLEX FORMATION BETWEEN POLY(ETHYLENE OXIDE) AND CATIONIC SURFACTANT AND TURBULENT WALL SHEAR STRESS IN AQUEOUS SOLUTION	52
5.1 Abstract	52
5.2 Introduction	52
5.3 Experimental	55
5.4 Results and Discussion	56
5.5 Conclusions	63
5.6 Acknowledgements	64
5.7 References	64
VI EFFECT OF POLY(ETHYLENE OXIDE) AND CATIONIC SURFACTANT COMPLEX STRUCTURE ON TURBULENT FRICTION FACTOR	81
6.1 Abstract	81
6.2 Introduction	81
6.3 Experimental	83
6.4 Results and Discussion	84
6.5 Conclusions	95
6.6 Acknowledgements	96
6.7 References	97
VII INFLUENCE OF POLYETHYLENE OXIDE ON THE RHEOLOGICAL PROPERTIES OF SEMI-DILUTE, WORMLIKE MICELLAR SOLUTIONS OF HEXADECYLTRIMETHYLAMMONIUM CHORIDE AND SODIUM SALICYLATE	116

CHAPTER	PAGE
7.1 Abstract	116
7.2 Introduction	117
7.3 Experimental	119
7.4 Results	120
7.5 Discussion and Conclusions	124
7.6 Acknowledgements	125
7.7 References	126
VIII CONCLUSIONS	142
REFERENCES	142
APPENDICES	146
Appendix A Viscosity Data for Aqueous PEO, HTAC, PEO-HTAC, PEO-HTAC-NaSal solutions at 30°C	146
Appendix B Static and Dynamic Light Scattering Aqueous PEO, HTAC, PEO-HTAC and PEO-HTAC-NaSal solutions at 30°C	160
Appendix C Surface tension and Conductivity Data for Aqueous HTAC and PEO-HTAC and PEO-HTAC-NaSal solutions at 30°C	204
Appendix D Rheological Data of Water at 30°C	227
Appendix E Rheological Data on Isotropic Phase of Wormlike Micelles in Aqueous Solutions Containing Cationic Surfactant, Sodium Salicylate and Poly(ethylene oxide)	229

CHAPTER	PAGE
Appendix F Critical Reynolds number, Re for Taylor Instability and Turbulent Flow Transition	237
Appendix G The number of polymer chains per one eddy at $Re = 5000$ for poly(ethylene oxide) in aqueous solutions at 30°C	243
CURRICULUM VITAE	245

LIST OF TABLES

TABLE		PAGE
CHAPTER I		
1.1	Drag reducing polymer fluids	1
1.2	Areas for the technical application of drag reducing additives	2
CHAPTER IV		
4.1	Viscosity data for aqueous PEO solutions at 30°C	39
4.2	Dynamic and static light scattering data for aqueous PEO solutions at 30°C	40
4.3	Conductivity and surface tension data for aqueous PEO/HTAC solutions at 30°C	41
CHAPTER V		
5.1	Conductivity and surface tension data of PEO-HTAC-NaCl complexes in quiescent aqueous solution at 30°C	66
5.2	Dynamic light scattering data of PEO – HTAC - NaCl complexes quiescent in aqueous solutions at 30°C	67
CHAPTER VI		
6.1	Various parameters obtained from viscosity and light scattering measurements at different molecular weights of PEO in aqueous solutions at 30°C	101
6.2	Various parameters obtained from light scattering measurement for HTAC, PEO-HTAC and PEO-HTAC-NaCl complex solutions at 30°C	102

TABLE

PAGE

CHAPTER VII

- | | | |
|-----|---|-----|
| 7.1 | Dependence of Temperature and HTAC concentration on various parameters determined from the analysis of rheological data for aqueous solutions of HTAC + NaSal without PEO where the mole ratio of $[\text{NaSal}]/[\text{HTAC}] = 1$ | 140 |
| 7.2 | Dependence of Temperature, PEO concentration and HTAC concentration on various parameters determined from the analysis of rheological data for aqueous solutions of HTAC + NaSal + PEO where the mole ratio of $[\text{NaSal}]/[\text{HTAC}] = 1$ | 141 |

LIST OF FIGURES

FIGURE	PAGE
CHAPTER IV	
4.1	44
<p>Dependence of wall shear stress, τ_w, on PEO concentrations for aqueous PEO solutions at 30°C, $Re = 2500$ and $Re = 5000$. (a) PEO1, $M_w = 0.91 \times 10^5$ g/mol; (b) PEO3, $M_w = 3.04 \times 10^5$ g/mol; (c) PEO6, $M_w = 6.06 \times 10^5$ g/mol; (d) PEO9, $M_w = 8.03 \times 10^5$ g/mol and (e) PEO20, $M_w = 17.9 \times 10^5$ g/mol.</p>	
4.2	45
<p>Plots of %DR versus $c[\eta]$ of PEO in aqueous solutions at different concentrations and molecular weights at 30°C: (a) $Re = 2500$; and (b) $Re = 5000$, PEO3 = PEO $M_w = 3.04 \times 10^5$ g/mol; PEO6 = PEO $M_w = 6.06 \times 10^5$ g/mol; PEO9 = PEO $M_w = 8.03 \times 10^5$ g/mol and PEO20 = PEO $M_w = 17.9 \times 10^5$ g/mol.</p>	
4.3	46
<p>Dependence of wall shear stress, τ_w, on HTAC concentrations at 30°C for aqueous HTAC solutions at $Re = 5000$.</p>	
4.4	47
<p>Dependence of wall shear stress, τ_w, on HTAC concentrations at 30 °C and $Re = 5000$ for solutions of: (a) HTAC/PEO1_40, PEO $M_w = 0.91 \times 10^5$ g/mol 40 ppm; (b) HTAC/PEO1_200, PEO $M_w = 0.91 \times 10^5$ g/mol 200ppm.</p>	
4.5	48
<p>Dependence of wall shear stress, τ_w, on HTAC concentrations 30°C and $Re = 5000$ for solutions of: (a) HTAC/PEO6_200, PEO $M_w = 6.06 \times 10^5$ g/mol 200 ppm; (b) HTAC/PEO20_200, PEO $M_w = 17.9 \times 10^5$ g/mol 200 ppm.</p>	

FIGURE	PAGE
4.6 Dependence of wall shear stress, τ_w , on HTAC concentrations 30 °C and $Re = 5000$ for solutions of: (a) HTAC/PEO6_40, PEO $M_w = 6.06 \times 10^5$ g/mol 40 ppm; (b) HTAC/PEO20_15, PEO $M_w = 17.9 \times 10^5$ g/mol 15 ppm.	49
4.7 Dependence of wall shear stress, τ_w , on PEO concentrations at 30°C and $Re = 5000$ for aqueous solutions of: (a) PEO6, PEO $M_w = 6.06 \times 10^5$ g/mol; (b) PEO6/HTAC_0.20, PEO $M_w = 6.06 \times 10^5$ g/mol and HTAC 0.20 mM.	50
4.8 Dependence of wall shear stress, τ_w , on PEO concentrations at 30°C and $Re = 5000$ for aqueous solutions of: (a) PEO20, PEO $M_w = 17.9 \times 10^5$ g/mol; (b) PEO20/HTAC_0.18, PEO $M_w = 17.9 \times 10^5$ g/mol and HTAC 0.18 mM.	51

CHAPTER V

5.1 Variation of the conductivity with surfactant concentration at 30°C for aqueous solutions of: (a) pure HTAC; (b) $[NaCl]/[HTAC] = 1/1$, the mole ratio of NaCl to HTAC equal to one; and (c) $[NaCl]/[HTAC] = 5/1$, the mole ratio of NaCl to HTAC equal to five.	69
5.2 Variation of the conductivity with surfactant concentration at 30°C for aqueous solutions of: (a) PEO6_40 + HTAC, PEO $M_w 6.06 \times 10^5$ g/mol, 40 ppm; (b) PEO6_40 + $[NaCl]/[HTAC] = 1/1$, PEO $M_w = 6.06 \times 10^5$ g/mol, 40 ppm, and the mole ratio of NaCl to HTAC equal to one; and (c) PEO6_40 + $[NaCl]/[HTAC] = 5/1$, PEO $M_w = 6.06 \times 10^5$ g/mol, 40 ppm, and the mole ratio of NaCl to HTAC equal to five.	71

FIGURE

PAGE

- 5.3 Variation of the conductivity with surfactant concentration at 30°C for aqueous solutions of: **(a)** PEO20_15 + HTAC, PEO $M_w=17.9 \times 10^5$ g/mol 15 ppm; **(b)** PEO20_15 + [NaCl]/[HTAC] = 1/1, PEO $M_w = 17.9 \times 10^5$ g/mol, 15 ppm, and the mole ratio of NaCl to HTAC equal to one; and **(c)** PEO20_15 + [NaCl]/[HTAC] = 5/1, PEO $M_w = 17.9 \times 10^5$ g/mol, 15 ppm, and the mole ratio of NaCl to HTAC equal to five. 73
- 5.4 Variation of the surface tension with surfactant concentration at 30°C for aqueous solutions of: **(a)** PEO6_40 + HTAC, PEO $M_w = 6.06 \times 10^5$ g/mol at 40 ppm; **(b)** PEO6_40 + [NaCl]/[HTAC] = 1/1, PEO $M_w = 6.06 \times 10^5$ g/mol, 40 ppm, and the mole ratio of NaCl to HTAC equal to one; and **(c)** PEO6_40 + [NaCl]/[HTAC] = 5/1, PEO $M_w = 6.06 \times 10^5$ g/mol, 40 ppm, and the mole ratio of NaCl to HTAC equal to five. 75
- 5.5 Dependence of wall shear stress, τ_w , on HTAC concentration of aqueous HTAC solutions with and without NaCl added at 30 °C, Re = 5000: **(a)** HTAC; **(b)** [NaCl]/[HTAC] = 1/1, the mole ratio of NaCl to HTAC equal to one; and **(c)** [NaCl]/[HTAC] = 5/1, the mole ratio of NaCl to HTAC equal to five. 76
- 5.6 Dependence of wall shear stress, τ_w , on HTAC concentration for aqueous PEO6_40+HTAC solutions with and without NaCl added at 30°C, Re = 5000: **(a)** PEO6_40 + HTAC, PEO $M_w 6.06 \times 10^5$ g/mol at 40 ppm; **(b)** PEO6_40 + [NaCl]/[HTAC] = 1/1, PEO $M_w 6.06 \times 10^5$ g/mol, 40 ppm, and the mole ratio of NaCl to HTAC equal to one; **(c)** [NaCl]/[HTAC] = 5/1, PEO $M_w 6.06 \times 10^5$ g/mol, 40 ppm, and the mole ratio of NaCl to HTAC equal to five. 77

FIGURE

PAGE

- 5.7 Dependence of wall shear stress, τ_w , on HTAC concentration for aqueous PEO20_15+HTAC solutions with and without NaCl added at 30 °C, $Re = 5000$. **(a)** PEO20_15 + HTAC, PEO M_w 17.9×10^5 g/mol, 15 ppm; **(b)** PEO20_15 + [NaCl]/[HTAC] = 1/1, PEO M_w 17.9×10^5 g/mol, 15 ppm, and the mole ratio of NaCl to HTAC equal to one; **(c)** [NaCl]/[HTAC] = 5/1, PEO M_w 17.9×10^5 g/mol, 15 ppm, and the mole ratio of NaCl to HTAC equal to five. 78
- 5.8 Dependence of wall shear stress, τ_w , on HTAC concentration for aqueous PEO20 + HTAC at MBC; PEO M_w 17.9×10^5 g/mol and HTAC = 0.2 mM solutions with and without NaCl added at 30 °C, $Re = 5000$. **(a)** PEO20 + HTAC 0.2 mM; **(b)** PEO20 + HTAC 0.2 mM + [NaCl]/[HTAC] = 1/1, the mole ratio of NaCl to HTAC equal to one; **(c)** PEO20 + HTAC 0.2 mM + [NaCl]/[HTAC] = 5/1, the mole ratio of NaCl to HTAC equal to five. 79
- 5.9 Schematic drawings of complexes formed in PEO + HTAC **(a)** in the absence and **(b)** in the presence of NaSal in aqueous solution, respectively, when HTAC concentration is above CMC. 80

CHAPTER VI

- 6.1 Friction factor, f versus Reynolds number, Re of water at 30°C. Re_c is the critical Reynolds number; Re_c of water at 30°C = 1,000. 103
- 6.2 Friction factor (f) vs. Reynolds number (Re) at various PEO concentrations of aqueous PEO solutions of PEO6, PEO M_w = 6.06×10^5 g/mol, at 30°C. 104

FIGURE

PAGE

CHAPTER VI

- 6.3 Friction factor (f) vs. Reynolds number (Re) at the optimum PEO concentrations of various PEO molecular weights at 30°C: (a) PEO1_50 ppm, PEO M_w 0.91×10^5 g/mol, 50 ppm; (b) PEO3_50 ppm, PEO M_w 3.04×10^5 g/mol, 50 ppm; (c) PEO6_40 ppm, PEO M_w 6.06×10^5 g/mol, 40 ppm; (d) PEO9_30 ppm, PEO M_w 8.03×10^5 g/mol, 30 ppm and (e) PEO20_15 ppm, PEO M_w 17.9×10^5 g/mol, 15 ppm. 105
- 6.4 Friction factor (f) vs. Reynolds number (Re) at various HTAC concentrations of aqueous HTAC solutions at 30°C. The critical micelle concentration, CMC of HTAC is 1.3 mM. 106
- 6.5.1 Friction factor (f) vs. Reynolds number (Re) at 30°C for aqueous solutions of: (a) water; (b) HTAC 5.0 mM; (c) HTAC 5.0 mM + $[NaCl]/[HTAC] = 5/1$. 107
- 6.5.2 Schematic drawings of micelle structures of (a) HTAC in aqueous solution and (b) HTAC in NaCl solution. 108
- 6.6.1 Friction factor (f) vs. Reynolds number (Re) at various HTAC concentrations and 30°C for aqueous solutions of HTAC/PEO1_200, PEO $M_w = 0.91 \times 10^5$ g/mol, 200 ppm. The critical micelle concentration, CMC of HTAC/PEO1_200 is 0.19 mM. MBC of HTAC/PEO1_200 is 1.80 mM and CAC of HTAC/PEO1_200 is 1.90 mM. 109
- 6.6.2 Schematic drawings of (a) PEO1 at 200 ppm in aqueous solution and (b) – (d) the complexes between PEO1 at 200 ppm and HTAC at various HTAC concentrations in aqueous solution. 110
- 6.7.1 Friction factor (f) vs. Reynolds number (Re) at various HTAC concentrations and 30°C for aqueous solutions of

- HTAC/PEO6_40, PEO $M_w = 6.06 \times 10^5$ g/mol, 40 ppm. The critical micelle concentration, CMC of HTAC/PEO6_40 is 0.18 mM. The maximum binding concentration, MBC of HTAC/PEO6_40 is 0.20 mM and the critical aggregate concentration, CAC of HTAC/PEO6_40 is 1.70 mM. 111
- 6.7.2 Schematic drawings of **(a)** PEO6 at 40 ppm in aqueous solution and **(b)** the complexes between PEO6 at 40 ppm and HTAC in aqueous solution. 112
- 6.8.1 Friction factor (f) vs. Reynolds number (Re) at 30°C for aqueous solutions of: **(a)** water; **(b)** PEO6_40 + HTAC 5.0 mM, PEO M_w 6.06×10^5 40 ppm and HTAC, 5.0 mM; **(c)** PEO6_40 + $[NaCl]/[HTAC] = 1/1$, PEO M_w 6.06×10^5 , 40 ppm, HTAC 5.0 mM and NaCl, 5.0 mM; **(d)** PEO6_40 + $[NaCl]/[HTAC] = 5/1$, PEO M_w 6.06×10^5 , 40 ppm, HTAC 5.0 mM and NaCl 25.0 mM. 113
- 6.8.2 Schematic drawings of **(a)** the complexes between PEO6 at 40 ppm and HTAC at 5.0 mM in aqueous solution and **(b)** the complexes between PEO6 at 40 ppm and HTAC at 5.0 mM in NaCl solution. 114
- 6.9 Friction factor (f) vs. Reynolds number (Re) at 30°C for aqueous solutions of: **(a)** water; **(b)** PEO6_40, PEO M_w 6.06×10^5 g/mol, 40 ppm; **(c)** HTAC 5.0 mM; **(d)** PEO6_40 + HTAC 5.0 mM, PEO M_w 6.06×10^5 g/mol, 40 ppm and HTAC 5.0 mM. 115

FIGURE

PAGE

CHAPTER VII

- 7.1 The effect of temperature on the frequency-dependent storage modulus, $G'(\omega)$ and loss modulus, $G''(\omega)$ is shown for aqueous solutions of HTAC 50 mM + NaSal 50 mM: **(a)** Without PEO and **(b)** With PEO 5 g/l: (Δ) G' at $T = 30^\circ\text{C}$;

- (▲) G'' at $T = 30^\circ\text{C}$; (▽) G' at $T = 40^\circ\text{C}$; (▼) G'' at $T = 40^\circ\text{C}$; (◇) G' at $T = 50^\circ\text{C}$ and (◆) G'' at $T = 50^\circ\text{C}$. 129
- 7.2 Cole-Cole plots of the loss modulus, G'' versus the storage modulus, G' together with fits of the low-frequency data to the Maxwell model at different temperatures for aqueous solutions of HTAC 50 mM + NaSal 50 mM: (a) No PEO and (b) With PEO 5 g/l: (□) 25°C ; (△) 30°C ; (▽) 40°C and (◇) 50°C . 130
- 7.3 Semilogarithmic plot of the average micellar length, \bar{L} (circle), the stress relaxation time, ($\tau_R = 1/\omega_{co}$) (square) and the zero shear viscosity, η_0 (triangle) versus $1000/T$ for the aqueous solutions of HTAC 50 mM + Nasal 50 mM: (○, □, △) No PEO and (●, ■, ▲) With PEO 5 g/l. 131
- 7.4 Dependence of storage modulus, G' and loss modulus, G'' on frequency, ω at different PEO concentrations for aqueous solutions of HTAC 50 mm + NaSal 50 mM + PEO of $M_w 1 \times 10^5$ g/mol at 30°C : (○) G' for PEO 1 g/l; (●) G'' for PEO 1 g/l; (□) G' for PEO 5 g/l; (■) G'' for PEO 5 g/l; (△) G' for PEO 10 g/l and (▲) G'' for PEO 10 g/l. 132
- 7.5 Reduced Cole-Cole plots of G''/G'_∞ versus G'/G'_∞ (scatter) together with low-frequency fits to the Maxwell model at different PEO concentrations for aqueous solutions containing 50 mM HTAC + 50 mM NaSal + PEO of $M_w 1 \times 10^5$ g/mol at 30°C : (○) PEO 1 g/l; (□) PEO 5 g/l and (△) PEO 10 g/l. 132

FIGURE

PAGE

7.6 Effect of HTAC concentration on $G'(\omega)$ and $G''(\omega)$ for aqueous solutions containing equimolar amounts of HTAC and NaSal at 30°C: **(a)** No PEO and **(b)** With 5 g/l PEO of $M_w = 1 \times 10^5$ g/mole: (○) G' for HTAC 25 mM; (●) G'' for HTAC 25 mM; (□) G' for HTAC 50 mM; (■) G'' for HTAC 50 mM; (△) G' for HTAC 100 mM; and (▲) G'' for HTAC 100 mM.

133

7.7 Reduced Cole-Cole plots of G''/G'_∞ , versus G'/G'_∞ (scatter) together with fits to the Maxwell model at different HTAC concentrations for equimolar NaSal/HTAC solutions without and with PEO of $M_w = 1 \times 10^5$ g/mol at 30°C: **(a)** No PEO and **(b)** With 5 g/l PEO: (i) HTAC = 25 mM; (ii) HTAC 50 mM and (iii) HTAC 100 mM.

134

ABBREVIATIONS

M_w	Molecular weight of sample
PEO	Poly(ethylene oxide)
PEO1	Poly(ethylene oxide) quoted $M_w = 1 \times 10^5$ g/mol
PEO3	Poly(ethylene oxide) quoted $M_w = 3 \times 10^5$ g/mol
PEO6	Poly(ethylene oxide) quoted $M_w = 6 \times 10^5$ g/mol
PEO9	Poly(ethylene oxide) quoted $M_w = 9 \times 10^5$ g/mol
PEO20	Poly(ethylene oxide) quoted $M_w = 4 \times 10^6$ g/mol
PEO1_40	PEO1 concentration of 40 ppm
HTAB, HTAC	Hexadecyltrimethylammonium Bromide and Chloride
CTAB, CTAC	Cetyltrimethylammonium Bromide and Chloride
NaSal	Sodium Salicylate
CMC	Critical Micelle Concentration
CAC	Critical Aggregate Concentration
MBC	Maximum Binding Concentration
SCU	Single Couette cell
DCU	Double Couette cell

LIST OF SYMBOLS

DR	Drag reduction
T	Temperature
R_{IB}	Inner radius of bob
R_{IC}	Inner radius of cup
R_{OB}	Outer radius of bob
R_{OC}	Outer radius of cup
L	Bob length
μ	Sample viscosity
ρ	Solvent density
ν	Kinematic viscosity
f	Friction factor of solution
f_0	Friction factor of solvent
τ_w	Wall shear stress
M_{DCU}	Total torque measuring from double Couette cell
M_{SCU}	Total torque measuring from single Couette cell
$\dot{\gamma}$	Shear rate
$\dot{\theta}$	Motor angular velocity
K_γ	Strain constant
K_τ	Stress Constant
[HTAC]/[NaSal]	The mole ratio of HTAC to NaSal
c_{PEO}^*	The optimum PEO concentration in aqueous solution of PEO
c_{HTAC}^*	The optimum HTAC concentration in aqueous solution of HTAC
$c_{HTAC/PEO}^*$	The optimum HTAC concentration in aqueous solution of PEO/HTAC complex
D_{app}	Apparent diffusion coefficient
D_{cm}	Center of mass diffusion coefficient
D_0	Infinite dilution diffusion coefficient
R_h	Hydrodynamic radius

R_g	Radius of gyration
η	Shear viscosity
η^*	Dynamic viscosity
η_{sp}	Specific viscosity
η_r	Reduced viscosity
η_0	Zero shear viscosity
G_0	Plateau shear modulus
G'	Storage Modulus
G''	Loss modulus
\tilde{G}_{min}	The dip of loss modulus in Cole-Cole plot
ω	Frequency
ω_{co}	Cross over frequency
τ_R	Relaxation time
τ_{rep}	Reptation time
τ_{br}	Mean waiting time for micelle of mean length \bar{L} to break into two pieces
l_e	Entanglement length
l_p	Persistence length
\bar{L}	Average micellar length