# RHEOLOGICAL AND OPTICAL PROPERTIES OF MIXTURES OF AMPHOLYTE AND FATTY ALCOHOL

Ms. Khin Thanda

,

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, and Case Western Reserve University 2000 ISBN 974-334-174-9

I19313263

Thesis title	: Rheological and Optical Properties of Mixtures of
	Ampholyte and Fatty Alcohol
By	: Ms. Khin Thanda
Program	: Polymer Science
Thesis Advisor	: Assoc. Prof. Anuvat Sirivat

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

College Director (Prof. Somchai Osuwan)

**Thesis Committee:** 

Armat Graval 28/4/2005

(Assoc. Prof. Anuvat Sirivat)

P.Sypyl.-

(Dr. Pitt Supaphol)

M. Dith. Thank

(Dr. Manit Nighitanakul)

#### ABSTRACT

#### 4172011063 : POLYMER SCIENCE PROGRAM

KEYWORD : Ampholyte/ Emulsion/ Zwitterionic surfactant
Khin Thanda: Rheological and Optical Properties of
Mixtures of Ampholyte and Fatty Alcohol.
Thesis Advisor: Assoc. Prof. Anuvat Sirivat, 80 pp.
ISBN 974-334-174-9

Structure and rheological properties of amphoteric surfactant-fatty alcohol mixtures, or emulsions, were investigated in terms of aging time, concentration, temperature and pH. Aging allowed a growth of the dispersed particles toward their equilibrium sizes after a period of 14 days. High concentrations of fatty alcohol induced the dispersed particles to aggregate. Both entanglement modulus and zero shear viscosity increased with fatty alcohol content until reaching their saturation values at which there was excess fatty alcohol. The increase in temperature above room temperature caused the emulsions to disaggregate. Zero shear viscosity and Bingham stress decreased with increasing temperature. However, an increase in temperature did not affect the storage entanglement modulus of the emulsions at high fatty alcohol concentrations. The amphoteric surfactant can be strongly influenced by pH effect. Entanglement modulus, zero shear viscosity and Bingham stress turned up the highest values at the isoelectric area of the surfactant molecules. Entanglement modulus, zero shear viscosity and Bingham stress decreased beyond the isoelectric regime due to hydrophilic repulsion between the surfactant molecules.

# ต้นฉบับ หน้าขาดหาย

#### ACKNOWLEDGEMENTS

This acknowledgement is gratefully made to all professors who so efficiently taught her at Petroleum and Petrochemical College, Chulalongkorn University.

The author greatly appreciates her research advisor Assoc. Prof. Anuvat Sirivat, who not only originated this thesis but also provided intensive counseling, constructive criticisms and suggestions. She is deeply indebted to her thesis committee members Dr. Pitt Supaphol and Dr. Manit Nithitanakul for proofread this manuscript and motivated to complete her thesis work.

Moreover, she would like to thank her beloved parents for their love, care, tenderness, understanding, encouragement and limitless sacrifice and advice. They have caused the author to concentrate on her future and have been a constant source of inspiration.

## TABLE OF CONTENTS

#### PAGE

i
iii
iv
v
vi
ix
х

### CHAPTER

I	INTRODUCTION	1
II	LITERATURE SURVEY	12
III	EXPERIMENTAL	17
	3.1 Materials	17
	3.2 Methodology	18
	3.2.1 Sample Preparation Of MUC32/FA Emulsions	18
	3.3 Apparatus	21
	3.3.1 du Nouy Pt Ring Tensiometer	21
	3.3.2 Zeta-potential Meter Systems 3.0+	21

IV

3.3.3 Optical Measure	ement	21
3.3.3.1 Optical	Microscope	21
3.3.3.2 Laser S	Scanning Microscope	22
3.3.4 Rheometer		25
3.3.4.1 Oscillato	ory Test	26
3.3.4.2 Steady S	State	26
RESULTS AND DISCU	SSION	27
4.1 Effect of Aging Time	On Emulsion Structure	28
4.1.1 Rheological Me	asurement	28
4.1.1.1 Viscos	ity As A Function Of Aging Time	28
4.1.1.2 Zero S	hear Viscosity	31
4.1.1.3 Storag	ge Modulus As A Function Of	
Aging	Time	32
4.1.1.4 Entang	glement Storage Modulus	35
4.1.1.5 Bingha	am Stress	36
4.1.2 Optical Measu	rement	37
4.2 Effect Of Fatty Alcoh	ol Concentration On Emulsion	
Structure		
4.2.1 Rheological M	easurement	41
4.2.1.1 Zero Sł	near Viscosity	41
4.2.1.2 Entang	lement Storage Modulus	42
4.2.1.3 Bingha	m Stress	43
4.2.2 Optical Measur	rement	44
4.3 Effect of Temperature	e On Emulsion Structure	47
4.3.1 Rheological M	easurement	47

V

## PAGE

	4.3.1.1 Zero Shear Viscosity	47
	4.3.1.2 Entanglement Storage Modulus	48
	4.3.1.3 Bingham Stress	49
4.3.2	Optical Measurement	50
4.4 Effec	t Of pH On Emulsion Structure	54
4.4.1	Characterization Of Surfactant	54
	4.4.1.1 Zeta-potential Measurement	54
4.4.2	Rheological Measurement	56
	4.4.2.1 Zero Shear Viscosity	56
	4.4.2.2 Entangle Storage Modulus	57
	4.4.2.3 Bingham Stress	58
4.4.3	Optical Measurement	59
CONCLI	USIONS	67
REFERE	INCES	69
APPEND	DICES	71

CURRICULUM VITAE	80

## LIST OF TABLES

#### TABLE

.

#### PAGE

4.1	Effect of Aging time	27
4.2	Effect of Fatty Alcohol Concentration	27
4.3	Effect of Temperature	27
4.4	Effect of pH	27

## LIST OF FIGURES

FIGURE		PAGE
1.1	Schematic representation of both O/W and W/O emulsions	2
1.2	Schematic of surfactant molecule (monomer)	9
1.3	A schematic illustration of surfactant association structures	10
3.1	The chemical structure of Miranol Ultra C32	17
3.2	Set-up of a laser scanning confocal microscope; light source	
	(LS), detector (D), pinhole (P), beam splitter (BS), objective	
	(O), focal plane (FP), specimen (S)	23
3.3	General overview of the laser scanning microscope	24
3.4	Principal features of cone-and-plate	25
4.1	Viscosity against shear rate as a function of aging time; (a)	
	MUC32:FA=1:2 (b) MUC32:FA=1:4 (c) MUC32:FA=1:6	
	(d) MUC32:FA=1:8, temperature = $26^{\circ}$ C, pH =8.7-9.2	29
4.2	Zero shear viscosity ( $\eta_0$ ) against aging time;	
	$\eta_0 = \eta$ at shear rate 0.01s <sup>-1</sup> , temperature =26°C, pH =8.7-9.2	31
4.3	Storage modulus against shear rate as a function of aging time	
	(a) MUC32:FA=1:2 (b) MUC32:FA=1:4 (c) MUC32:FA=1:6	
	(d) MUC32:FA=1:8, temperature = $26^{\circ}$ C, pH =8.7-9.2	33
4.4	Entanglement storage modulus (G <sup>0</sup> <sub>N</sub> ) against	
	aging time; $G_N^0$ was G' at 100 rad/s, strain = 0.2%,	
	temperature = $26 \pm 1^{\circ}$ C, pH = 8.7-9.2	35
4.5	Bingham stress ( $\tau_B$ ) against aging time; temperature =26±1 <sup>o</sup> C,	
	pH = 8.7-9.2	36

4.6 Micrographs of emulsion obtained at 100 magnification as a function of aging time (a) MUC32:FA=1:2 at 1 day (b) MUC32:FA=1:2 at equilibrium (c) MUC32:FA=1:4 at 1day (d)MUC32:FA=1:4 at equilibrium (e) MUC32:FA=1:6 at equilibrium (f) MUC32:FA=1:8 at 1 day (g) MUC32:FA=1:8 at equilibrium; temperature =  $26 \pm 1^{\circ}$ C, pH = 8.7-9.2 38 4.7 Micrographs of emulsion obtained at 1000 magnification as a function of aging time (a) MUC32:FA=1:2 at 1 day (b) MUC32:FA=1:2 at equilibrium (c) MUC32:FA=1:4 at Iday (d)MUC32:FA=1:4 at equilibrium (e) MUC32:FA=1:6 at equilibrium (f) MUC32:FA=1:8 at 1 day (g) MUC32:FA=1:8 at equilibrium; temperature was  $26\pm1^{\circ}$ C and pH was in the range of 8.7-9.2 40 4.8 Zero shear viscosity ( $\eta_0$ ) against fatty alcohol concentration;  $\eta_0 = \eta$  at shear rate 0.01s<sup>-1</sup>, temperature =26<sup>o</sup>C, pH =8.7-9.2 41 4.9 Entanglement storage modulus  $(G^0_N)$  against fatty alcohol concentration;  $G^0_N$  was G' at 100 rad/s, strain = 0.2%, temperature =  $26 \pm 1^{\circ}$ C, pH = 8.7-9.2 42 4.10 Plot of Bingham stress ( $\tau_B$ ) against fatty alcohol concentration; temperature= $26 \pm 1^{\circ}$ C, pH=8.7-9.243 4.11 Micrographs of emulsion obtained at 100 magnification as a function of fatty alcohol concentration (a) MUC32:FA=1:2 (b) MUC32:FA=1:4 (c) MUC32:FA=1:6 (d)MUC32:FA=1:8; temperature =  $26 \pm 1^{\circ}$ C, pH = 8.7-9.2 45

GURE	PAGE
4.12 The 1000 magnification micrographs of emulsion as a function of fatty alcohol concentration (a) MUC32:FA=1:2	2

	(b) MUC32:FA=1:4 (c) MUC32:FA=1:6 (d)MUC32:FA=1:8;	
	temperature = $26 \pm 1^{\circ}$ C, pH = 8.7-9.2	46
4.13	Zero shear viscosity ( $\eta_0$ ) against temperature;	
	$\eta_0 = \eta$ at shear rate 0.01s <sup>-1</sup> , temperature = 26, 35, 55 <sup>o</sup> C,	
	pH =8.7-9.2	47
4.14	Entanglement storage modulus (G <sup>0</sup> <sub>N</sub> ) against temperature;	
	$G_{N}^{0}$ was G' at 100 rad/s, strain = 0.2%, temperature = 26, 35,	
	$55^{\circ}$ C, pH = 8.7-9.2	48
4.15	Bingham stress ( $\tau_B$ ) against temperature; temperature=26, 35,	
	55°C, pH=8.7-9.2	49
4.16	Micrographs of emulsion obtained at 1000 magnification of	
	MUC32:FA=1:2% by weight as a function of temperature	
	(a) $26^{\circ}C$ (b) $35^{\circ}C$ (c) $55^{\circ}C$ , pH = 8.7-9.2	51
4.17	Micrographs of emulsion obtained at 1000 magnification of	
	MUC32:FA=1:4% by weight as a function of temperature	
	(a) $26^{\circ}$ C (b) $35^{\circ}$ C (c) $55^{\circ}$ C, pH = 8.7-9.2	52
4.18	Micrographs of emulsion obtained at 1000 magnification of	
	MUC32:FA=1:8% by weight as a function of temperature	
	(a) $26^{\circ}$ C (b) $35^{\circ}$ C (c) $55^{\circ}$ C, pH = 8.7-9.2	53
4.19	Zeta-potential against surfactant concentration and pH	
	as a function of pH; temperature = $26 \pm 1^{\circ}$ C	54
4.20	Zero shear viscosity ( $\eta_0$ ) against pH; $\eta_0 = \eta$ at shear rate	
	$0.01s^{-1}$ , temperature = 5,7,8.5-9.2 and 10	56

.

xii

FIGU	RE	PAGE
4.21	Entanglement storage modulus (G <sup>0</sup> <sub>N</sub> ) against pH;	
	$G_{N}^{0}$ was G' at 100 rad/s, strain = 0.2%, temperature = $26 \pm 1^{0}$ C,	
	pH = 5, 7, 8.7-9.2 and 10	57
4.22	Bingham stress ( $\tau_B$ ) against pH; temperature=26±1 <sup>0</sup> C,	
	pH=5, 7, 8.7-9.2 and 10	58
4.23	Schematic drawing showing variation in ionic charge	
	and closeness of packing for amphoteric surfactant at	
	varying pH	60
4.24	Micrographs of emulsion obtained at 100 magnification of	
	MUC32:FA=1:2% by weight as a function of pH;	
	(a) $pH = 5$ (b) $pH = 7$ (c) $pH = 10$ , temperature $= 26 \pm 1^{0}C$	61
4.25	Micrographs of emulsion obtained at 100 magnification of	
	MUC32:FA=1:4% by weight as a function of pH;	
	(a) pH = 5 (b) pH = 7 (c) pH = 10, temperature = $26 \pm 1^{\circ}C$	62
4.26	Micrographs of emulsion obtained at 100 magnification of	
	MUC32:FA=1:6% by weight as a function of pH;	
	(a) $pH = 5$ (b) $pH = 7$ (c) $pH = 10$ , temperature $= 26 \pm 1^{\circ}C$	63
4.27	Micrographs of emulsion obtained at 100 magnification of	
	MUC32:FA=1:2% by weight as a function of pH;	
	(a) $pH = 5$ (b) $pH = 7$ (c) $pH = 10$ , temperature $= 26 \pm 1^{\circ}C$	64
4.28	Micrographs of emulsion obtained at 1000 magnification of	
	MUC32:FA=1:2% by weight as a function of pH;	
	(a) $pH = 5$ (b) $pH = 7$ (c) $pH = 10$ , temperature $=26 \pm 1^{\circ}C$	65
4.29	Micrographs of emulsion obtained at 1000 magnification of	
	MUC32:FA=1:6% by weight as a function of pH;	
	(a) $pH = 5$ (b) $pH = 7$ (c) $pH = 10$ , temperature $= 26 \pm 1^{\circ}C$	66