

**USE OF COACERVATE PHASE TO EXTRACT THE AROMATIC
SOLUTES FROM WASTEWATER BY USING A NONIONIC SURFACTANT**



Ms. Punjaporn Trakultamupatam

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

2002

ISBN 974-17-1395-9

Thesis Title : Use of Coacervate Phase to Extract the Aromatic
Solute from Wastewater by Using A Nonionic
Surfactant
By : Punjaporn Trakultamupatam
Program : Petrochemical Technology
Thesis Advisors : Prof. Somchai Osuwan
Prof. John F. Scamehorn

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
.....
(Assoc. Prof. Kunchana Bunyakiat)

S. Osuwan
.....
(Prof. Somchai Osuwan)

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

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

Edgar A. O' Rear
.....
(Prof. Edgar A. O' Rear)

Boonyarach Kitiyanan
.....
(Dr. Boonyarach Kitiyanan)

ABSTRACT

4081002063 : PETROCHEMICAL TECHNOLOGY PROGRAM

Punjaborn Trakultamupatam: Use of Coacervate Phase to Extract the Aromatic Solutes from Wastewater by Using A Nonionic Surfactant.

Thesis Advisors: Prof. Somchai Osuwan and Prof. John F. Scamehorn, 108 pp. ISBN 974-17-1395-9

Keywords: cloud point/ extraction/ coacervate/ micellar-rich phase/ nonionic surfactant/ phase separation/ rotating disc contactor

The cloud point extraction (CPE) of aromatic contaminants (benzene, toluene and ethylbenzene) from wastewater was studied as batch experiments in laboratory scale and continuous operation in a pilot scale, differential extractor. An environmentally friendly nonionic surfactant was utilized as a separating agent. When the temperature of the nonionic surfactant micellar solution is greater than its cloud point, the solution will separate into two aqueous phases known as the micellar-rich phase or coacervate phase, and the micellar-dilute phase. The organic solutes contained in the solution tend to solubilize into the micelles and mostly concentrate into the coacervate phase, leaving the dilute phase with a low concentration of solutes as the purified water. In batch experiments, several vials capped with septa containing nonionic surfactant, aromatic solute, and water with and without added electrolyte (NaCl) were placed in an isothermal water bath until equilibrium was reached. After phase separation occurred, the relative phase volumes of each phase were measured. The concentrations of nonionic surfactant and aromatic solute in the micellar-rich phase and the micellar-dilute phase were analyzed. The results showed that temperature, NaCl concentration and degree of alkylation of the aromatic solutes enhance the solute partition ratio, leading to a higher solute concentration in the micellar-rich phase. In continuous operation, a pilot scale, temperature controllable rotating disc contactor (RDC) was fabricated. The polluted water and nonionic surfactant solution were fed counter-currently to the column as feed and solvent, respectively. The phase separation occurred inside the column. The concentrations of nonionic surfactant and aromatic solute in the

coacervate stream and the micellar-dilute phase stream were analyzed. The concentration of solute in the coacervate phase increases as temperature, rotation speed of the rotor disc, NaCl concentration, wastewater/surfactant solution flowrate ratio and degree of alkylation of the aromatic solutes increase. The overall volumetric mass transfer coefficient and the number of transfer unit in the RDC increase with increasing temperature and rotation speed of the rotor disc. In pilot scale, multistage, continuous extractor, the toluene partition ratio and concentration of toluene in the coacervate phase are two times greater than that observed in a single stage, equilibrium batch experiment with the same initial condition.

บทคัดย่อ

ปัญญพร ตระกูลถ้ำอุปถัมภ์ : การแยกสกัดสารอะโรเมติกส์ออกจากน้ำเสียโดยอาศัยการแยกวัฏภาคของสารลดแรงตึงผิวชนิดไม่มีประจุ (Use of Coacervate Phase to Extract the Aromatic Solutes from Wastewater by Using A Nonionic Surfactant) อ. ที่ปรึกษา : ศ. ดร. สมชาย โอสุวรรณ และ ศ. ดร. จอห์น สแกมเมอร์ 108 หน้า ISBN 974-17-1395-9

การสกัดแบบขุ่นถูกนำมาใช้เพื่อแยกสกัดสารประกอบอะโรเมติกส์ออกจากน้ำเสียโดยศึกษาทั้งการสกัดแบบกะในหลอดทดลองและการสกัดแบบต่อเนื่องในเครื่องสกัดนาร่องแบบดิฟเฟอร์เรนเชียล สารที่ใช้ในการแยกคือสารลดแรงตึงผิวชนิดไม่มีประจุซึ่งเป็นสารที่ไม่ก่อให้เกิดอันตรายต่อสิ่งแวดล้อม เมื่อสารละลายของสารลดแรงตึงผิวชนิดไม่มีประจุมีอุณหภูมิสูงกว่าจุดขุ่นสารละลายจะแยกออกเป็นสองวัฏภาค ได้แก่ วัฏภาคที่มีไมเซลล์เป็นจำนวนมากหรือวัฏภาคโคเอกเซอร์เวท และวัฏภาคที่มีไมเซลล์เป็นจำนวนน้อย ตัวถูกละลายอินทรีย์ที่อยู่ในสารละลายจะละลายเข้าไปในไมเซลล์และมีความเข้มข้นสูงอยู่ในวัฏภาคโคเอกเซอร์เวท ทำให้วัฏภาคที่มีไมเซลล์เป็นจำนวนน้อยเปรียบเสมือนเป็นน้ำที่มีความบริสุทธิ์มากขึ้นเนื่องจากมีความเข้มข้นของตัวถูกละลายต่ำ ในการทดลองแบบกะสารละลายที่ประกอบด้วยสารลดแรงตึงผิวชนิดไม่มีประจุ ตัวถูกละลายอะโรเมติกส์ ทั้งที่มีการเติมเกลือและไม่มีการเติมเกลือถูกเตรียมในขวดเก็บตัวอย่างแล้วปิดด้วยฝาเซปตัมก่อนนำไปแช่ในอ่างควบคุมอุณหภูมิจนถึงสภาวะสมดุลจึงทำการวัดปริมาตรสัมพัทธ์ ความเข้มข้นของสารลดแรงตึงผิวและตัวถูกละลายอะโรเมติกส์ในแต่ละวัฏภาค ผลการทดลองพบว่าอุณหภูมิ ความเข้มข้นของเกลือ และองค์การเติมหมู่แอลคิลของตัวถูกละลายอะโรเมติกส์ช่วยเพิ่มสัดส่วนการละลายของตัวถูกละลายอะโรเมติกส์ในวัฏภาคโคเอกเซอร์เวท ส่งผลให้ความเข้มข้นของตัวถูกละลายอะโรเมติกส์ในวัฏภาคโคเอกเซอร์เวทสูงขึ้น เครื่องสกัดแบบโรเทตติ้งดิสก์คอนแทคเตอร์ถูกสร้างขึ้นในขนาดนาร่องเพื่อใช้ในการทดลองแบบต่อเนื่อง ในหอสกัดนี้ น้ำเสียและสารละลายของสารลดแรงตึงผิวชนิดไม่มีประจุถูกป้อนเข้าไปแบบสวนทางกันและ การแยกวัฏภาคเกิดขึ้นภายในหอสกัด หลังจากนั้นทำการวิเคราะห์ความเข้มข้นของสารลดแรงตึงผิวและตัวถูกละลายอะโรเมติกส์ในแต่ละวัฏภาค ผลการทดลองพบว่าเมื่ออุณหภูมิ ความเร็วรอบการกวน อัตราส่วนอัตราการไหลของน้ำเสียต่อสารละลายของสารลดแรงตึงผิวและองค์การเติมหมู่แอลคิลของตัวถูกละลายอะโรเมติกส์เพิ่มขึ้น มีผลให้ความเข้มข้นของตัวถูกละลายในวัฏภาคโคเอกเซอร์เวทสูงขึ้น ค่าสัมประสิทธิ์รวมการถ่ายโอนมวล และจำนวนหน่วยการถ่ายโอนในเครื่องสกัดแบบโรเทตติ้งดิสก์คอนแทคเตอร์สูงขึ้นเมื่อเพิ่มอุณหภูมิและความเร็วรอบของจานหมุน นอกจากนี้

นั้นยังพบว่าเมื่อทำการทดลองที่สภาวะเริ่มต้นแบบเดียวกัน ค่าสัดส่วนการละลายและความเข้มข้นของโพลีเมอร์ในวัฏภาคโคแอคเซอร์เวทที่ได้จากการทดลองแบบต่อเนื่องในเครื่องสกัดแบบหลายชั้นตอนสูงกว่าค่าที่ได้จากการทดลองแบบกะชั้นตอนเดียวที่สภาวะสมดุลถึงสองเท่า

ACKNOWLEDGEMENTS

First and foremost, I would like to give my thankfulness to The Thailand Research Fund (TRF) under the Royal Golden Jubilee Ph.D. program for financial support. Moreover, the Basic Research Grant for Royal Golden Jubilee Ph.D. Program provides an extra funding.

I would like to express my sincere thanks to Prof. Somchai Osuwan and Prof. John F. Scamehorn for giving me a privilege opportunity to work with them.

Prof. Somchai Osuwan always provides me a constant support, advice and encouragement throughout the course of my graduate work. His generosity and supports are aimed not only at my academia but also my personal way of life. His boundless enthusiasm has enabled me to attend a number of excellent international conferences, which allow me to open my vision both for future career and life experience. I also wish to thank for his consistent attentions on my research. His discernment and meaningful guidance and comments are invaluable.

I would like to express my gratitude to Prof. John F. Scamehorn for his creative and sharp advocacy. Without his insight knowledge, this research might not be accomplished. I also wish to thank for his willingness to train me to be a practicing researcher. His discussion and criticism are greatly useful. I am extremely grateful for his patience working on several papers. My writing skills are developed by his kind help. Moreover, I really appreciate his hospitality during my visits at The University of Oklahoma.

I would like to acknowledge Mr. Sanit Prinakorn for his countless assistance on my extractor. He is a really good technician. I have never met a person who practically knows how to adapt things effectively like him. He taught me a lot of hardware skills. I am sure that the extractor would not be successfully fabricated without his help.

I would like to give my thankfulness to Prof. Edgar A. O' Rear and Dr. Boonyarach Kitiyanan for being my thesis committee, PPC faculties for their guidance and support; PPC staffs for their contributions. Gratitude is also passed to my friends especially Mr. Siriphong Roatluechai, Ms. Apanee Luengnaruemitchai, Ms. Chalothorn Soponvuttikul and PPC students class' 97 for their sincere friendship, love and encouragement.

Last but not least, I would like to express my deep grateful to my parents, brother and sister. Without their love and understanding, I would not be able to achieve my goal. Thank you for supporting me in every way. I also wish to thank my supportive husband who has never given up encouraging me throughout my study.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	v
Acknowledgement	vii
Table of Contents	ix
List of Tables	xii
List of Figures	xiii

CHAPTER

I	INTRODUCTION	1
	Background	2
	Objectives	4
	Preliminary Study on the CPE of Chlorinated Hydrocarbon	5
II	REMOVAL OF VOLATILE AROMATIC CONTAMINANTS FROM WASTEWATER BY CLOUD POINT EXTRACTION	10
	Abstract	11
	Introduction	12
	Background	13
	Experimental	16
	Results and Discussion	18
	Acknowledgements	23
	References	24
III	SCALING UP CLOUD POINT EXTRACTION OF AROMATIC CONTAMINANTS FROM WASTEWATER IN A CONTINUOUS ROTATING DISC CONTACTOR:	

CHAPTER	PAGE
PART 1. EFFECT OF DISC ROTATION SPEED AND WASTEWATER/SURFACTANT RATIO	33
Abstract	34
Introduction	35
Background	37
Experimental	40
Results and Discussion	43
Acknowledgements	48
References	49
IV SCALING UP CLOUD POINT EXTRACTION OF AROMATIC CONTAMINANTS FROM WASTEWATER IN A CONTINUOUS ROTATING DISC CONTACTOR: PART 2. EFFECT OF OPERATING TEMPERATURE AND ADDED ELECTROLYTE	60
Abstract	61
Introduction	62
Background	63
Experimental	66
Results and Discussion	69
Acknowledgements	73
References	74
V CONCLUSIONS AND RECOMMENDATIONS	84
REFERENCES	87
APPENDIX	89
Use of a Surfactant Coacervate Phase to Extract Chlorinated Aliphatic Compounds from Water: Extraction of Chlorinated	

CHAPTER	PAGE
Ethanes and Quantitative Comparison to Solubilization in Micelles	
CURRICULUM VITAE	107

LIST OF TABLES

TABLE		PAGE
Chapter I		
1	Cloud points of 50 mM OP(EO) ₇ system	8
2	Liquid-coacervate extraction data : initial [OP(EO) ₇] = 50 mM, initial [solute] = 1.0 mM	9
Chapter II		
1	Cloud points of 70 mM OP(EO) ₇ system	28
Appendix		
1	CMC of surfactants with no organic solutes	100
2	Cloud points of 50 mM OP(EO) ₇ system	101
3	Liquid-coacervate extraction data : initial [OP(EO) ₇] = 50 mM, initial[solute] = 1.0 mM	102
4	Semiequilibrium dialysis data for micellar solubilization of 50 mM OP(EO) ₉ and 1.0 mM organic solute initial retentate concentrations	103
5	Summary of partitioning and solubilization parameters for the solute	104

LIST OF FIGURES

FIGURE	PAGE
Chapter I	
1	Schematic of liquid-coacervate extraction 7
Chapter II	
1	Surfactant concentration in coacervate phase as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte) 29
2	Fractional coacervate volume as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte) 29
3	Surfactant partition ratio as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte) 30
4	Benzene partition ratio as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte) 30
5	Percentage of benzene extracted in coacervate phase as a function of total surfactant concentration and temperature (system: 100 ppm benzene without added electrolyte) 31
6	Benzene partition ratio and percentage of benzene extracted in coacervate phase as a function of NaCl concentration (system: 100 ppm benzene, 70 mM surfactant, and 30 °C) 31
7	Partition ratio of several aromatic solutes as a function of temperature (system: 100 ppm aromatic solutes, 70 mM surfactant without added electrolyte) 32
8	Schematic of integrated process including a multistage cloud point

FIGURE	PAGE
extractor and vacuum stripper	32
 Chapter III 	
1 A schematic diagram of the cloud point extraction unit	53
2 Phenol concentration in dilute phase stream as a function of Operating time (system: 500 ppm phenol, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C)	53
3 Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C)	54
4 Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C)	54
5 Surfactant and toluene partition ratio as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C)	55
6 Fraction of total surfactant present and fraction of toluene extracted in coacervate stream as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C)	55
7 Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C)	56
8 Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant	

FIGURE	PAGE
<p>solution, 150 rpm agitator speed, and 40 °C)</p> <p>9 Surfactant and toluene partition ratio as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 mM surfactant solution, 150 rpm agitator speed, and 40 °C)</p>	56
<p>10 Fraction of total surfactant present and fraction of toluene extracted in coacervate stream as a function of wastewater/surfactant solution flowrate ratio (system: 100 ppm toluene, 300 Mm surfactant solution, 150 rpm agitator speed, and 40 °C)</p>	57
<p>11 Comparison of surfactant and solute partition ratio and fraction of solute extracted in coacervate stream between toluene and ethylbenzene (system: 100 ppm solute, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C)</p>	58
<p>12 Number of transfer unit (NTU) and height of transfer unit (HTU) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C)</p>	58
<p>13 Overall volumetric mass transfer coefficient (Ka) as a function of agitator speed (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 40 °C)</p>	59
<p>14 Comparison of surfactant and toluene concentration in coacervate stream (c) and partition ratio between a single stage equilibrium batch and continuous operation (system: batch; 3.75 wt % surfactant, 100 ppm toluene, and 40 °C. continuous; 2.03 wt % surfactant, 100 ppm toluene, 6.9/1 wastewater/surfactant flowrate ratio, 150 rpm agitator speed, and 40 °C)</p>	59

FIGURE		PAGE
Chapter IV		
1	A schematic diagram of the cloud point extraction unit	78
2	Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitator speed)	78
3	Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitator speed)	79
4	Surfactant and toluene partition ratio as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitator speed)	79
5	Fraction of total surfactant present and fraction of toluene extracted in coacervate stream as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, and 150 rpm agitation speed)	80
6	Surfactant concentration in coacervate stream (c) and dilute phase stream (d) as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C)	80
7	Toluene concentration in coacervate stream (c) and dilute phase stream (d) as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C)	81
8	Surfactant and toluene partition ratio as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator	

FIGURE	PAGE
speed, and 40 °C)	81
9 Fraction of total surfactant present and fraction of toluene extracted in coacervate stream as a function of NaCl concentration (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitation speed, and 40 °C)	82
10 Number of transfer unit (NTU) and height of transfer unit (HTU) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C)	82
11 Overall volumetric mass transfer coefficient (Ka) as a function of temperature (system: 100 ppm toluene, 300 mM surfactant solution, 6.9/1 wastewater/surfactant solution flowrate ratio, 150 rpm agitator speed, and 40 °C)	83
Appendix	
1 Schematic of semi-equilibrium dialysis	105
2 Schematic of liquid-coacervate extraction	106