IONIC-LIQUID BASED SEPARATION OF AZEOTROPIC MIXTURES

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ABSTRACT

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A methodology for screening of ionic liquids (ILs) as entrainers and for design of ILs-based separation processes in various homogeneous binary azeotropic mixtures is presented through two case studies: ethanol + water and isopropanol + water. ILs as entrainers were screened based on a combination of criteria such as stability, toxicity, environmental impacts, their miscibility in the target solute component (water) and their Hildebrand solubility parameter group contribution. The best candidates for the aqueous systems were selected, namely 1-Ethyl-3-Methylimidazolium Ethylsulfate [C_2MIM][$EtSO_4$], 1-Ethyl-3-Methylimidazolium Dicyanamide [C_2MIM][$N(CN)_2$], 1-Ethyl-3-Methylimidazolium Acetate [C_2MIM][Ac], and 1,3-Dimethylimidazolium Dimethyl phosphate [C_1MIM][DMP]. Extractive distillation with a solvent recovery was simulated in Pro II simulator to evaluate the energy requirement to obtain 99.8%mol purity of alcohol. Based on minimum energy requirement of each IL entrainer, [C_1MIM][DMP] was chosen as the final candidate for the ethanol + water, given an energy savings of 22% compared to the conventional solvent (Ethylene glycol). The design flexibility for azeotropic separation process with the same ILs entrainer, product purity, and designed parameters was investigated for the isopropanol + water azeotrope. [C_1MIM][DMP] was excluded since the extraction with [C_1MIM][DMP] could not give 99.8%mol purity of the alcohol with a reasonable number of theoretical stages. By fixing all design parameters with the same [C_2MIM][$N(CN)_2$] as entrainer, an increase in size of alcohol from ethanol to isopropanol gives a lower overall energy consumption because the isopropanol + water had a weaker interaction than the ethanol + water leading to the easier to extract water from isopropanol than extracting of water from ethanol.

บทคัดย่อ

กุสุมา กุละจันทร์เพ็ง: การแยกของผสมอะซิโอทอรปด้วยของเหลวไอออนิก (Ionic-Liquid Based Separation of Azeotropic Mixtures) อ. ที่ปรึกษา: ดร. อุทัยพร สุริยประภาดิลก และ ศ.ดร. ราฟิก กานี่ 186 หน้า

วิธีการสำหรับการคัดเลือกของเหลวไอออนิกเป็นสารช่วยกลั่น (entrainers) และการออกแบบกระบวนการแยกโดยใช้ของเหลวไอออนิกใช้ในหลากหลายระบบของผสมอะซิโอทอรปสององค์ประกอบที่เป็นเนื้อเดียวกันถูกนำเสนอในงานวิจัยนี้ ผ่านสองกรณีศึกษาคือเอทานอล + น้ำ และ ไอโซโพรพานอล + น้ำ ของเหลวไอออนิกถูกคัดเลือกจากหลักเกณฑ์ดังนี้คือความเสถียร ความเป็นพิษ ผลกระทบต่อสิ่งแลดล้อม การผสมเข้ากันได้กับน้ำและพารามิเตอร์การละลาย (Hildebrand solubility parameter group contribution) ของของเหลวไอออนิก จากการศึกษาพบว่าของเหลวไอออนิกที่ดีที่สุดสำหรับระบบที่ประกอบด้วยน้ำคือ 1-Ethyl-3-Methylimidazolium Ethylsulfate [C_2MIM][$EtSO_4$], 1-Ethyl-3-Methylimidazolium Dicyanamide [C_2MIM][$N(CN)_2$], 1-Ethyl-3-Methylimidazolium Acetate [C_2MIM][Ac], และ 1,3-Dimethylimidazolium Dimethyl phosphate [C_1MIM][DMP] กระบวนการกลั่นสกัดด้วยการนำสารละลายกลับมาใช้ใหม่ถูกจำลองขึ้นด้วยโปรแกรมจำลองทางคอมพิวเตอร์ (Pro II) เพื่อประเมินการใช้พลังงานของกระบวนการแยกให้ได้แอลกอฮอล์บริสุทธิ์ 99.8 % จากการศึกษาพบว่า [C_1MIM][DMP] ถูกเลือกเป็นสารช่วยกลั่นสำหรับการแยกเอทานอล + น้ำ บนพื้นฐานของการใช้พลังน้อยที่สุดซึ้งสามารถลดพลังงานได้ถึง 22 % เมื่อเปรียบเทียบกับการใช้สารละลายโดยทั่วไป (Ethylene glycol) ความยืดหยุ่นในการออกแบบสำหรับกระบวนการแยกของผสมอะซิโอทอรปด้วยของของเหลวไอออนิกตัวเดิมความบริสุทธิ์ของผลิตภัณฑ์และพารามิเตอร์ในการออกแบบเหมือนเดิมกับการแยกเอทานอล + น้ำ ถูกศึกษา สำหรับของผสมอะซิโอทอรป ไอโซโพรพานอล + น้ำ ผลการศึกษาแสดงให้เห็นว่า [C1MIM][DMP] ไม่สามารถทำให้แอลกอฮอล์บริสุทธิ์ 99.8 % เนื่องจากจำนวนชั้นของหอกลั่นที่ใช้มากเกินไป โดยการกำหนดพารามิเตอร์การออกแบบทั้งหมดให้เหมือนกับระบบที่ใช้ [C_2MIM][$N(CN)_2$] เป็นสารช่วยกลั่น พบว่าการเพิ่มขึ้นของจำนวนอะตอมของคาร์บอนในแอลกอฮอล์จากเอทานอลเป็นไอโซโพรพานอล ส่งผลให้พลังงานที่ใช้ทั้งหมดลดลงเพราะว่าไอโซโพรพานอลกับน้ำมีปฏิสัมพันธ์ระหว่างกันที่อ่อนกว่าเอทานอลกับน้ำ ดังนั้นการสกัดน้ำออกจากไอโซโพรพานอลจึงทำได้ง่ายกว่าการสกัดน้ำออกจากเอทานอล

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TABLE OF CONTENTS

		PAGE
Title Page		i
Abstract (in English)		iii
Abstract (in Thai)		iv
Acknowledgements		v
Table of Contents		vi
List of Tables		ix
List of Figures		xiv
Abbreviations		xxiii
List of Symbols		xxvi
CHAPTER		
I	**INTRODUCTION**	1
II	**LITERATURE REVIEW**	3
	2.1 Azeotropes	
	2.1.1 Definition of Azeotropes	3
	2.1.2 Conditions for the Occurrence of Azeotropic Behavior	3
	2.1.3 Type of Azeotropic Systems	4
	2.1.4 Homogeneous and Heterogeneous Azeotropes	6
	2.1.5 Separation of Azeotropic Mixtures	8
	2.2 Ionic Liquid	8
	2.2.1 Definition of Ionic Liquids	8
	2.2.2 Structure of Ionic Liquid	8
	2.2.3 Attraction of Ionic Liquid	9
	2.2.4 Ionic Liquid as Entrainers	11
	2.3 Group Contribution Methods	13
	2.3.1 Solubility Parameter	13
	2.3.2 Liquid Density of Ionic Liquids	15

CHAPTER PAGE

2.3.3 Heat Capacity Estimation of Ionic Liquids 18
2.4 Computer Aided Molecular Design (CAMD) Method 20
2.5 Predictive Thermodynamic Models 22
2.5.1 COSMO-RS Model 22
2.5.2 UNIFAC Models 23
2.5.3 NRTL Model 25
2.6 Extractive Distillation with Ionic Liquids 26
2.6.1 Aqueous Systems 27
2.6.2 Non-Aqueous Systems 39

III METHODOLOGY 44
3.1 Equipment and Software 44
3.2 Methodology 44
3.2.1 Literature Survey Study 44
3.2.2 Designing and Screening Ionic Liquid Candidates 45
3.2.3 Conceptual Process Design and Simulate Process 45
3.2.4 Validation 45

IV RESULTS AND DISCUSSION 46
4.1 Extended Hildebrand Solubility Parameter Group Contribution 46
4.2 A Systematic Methodology for the Screening of ILs As Entrainers and the Design of ILs-Based Separation Processes 49
4.2.1 Step-1 : Stability of the Ionic Liquid 51
4.2.2 Step-2 : Miscibility of the Ionic Liquid and Target Component 52
4.2.3 Step-3 : Design and Simulation of Separation Feasibility and Energy Requirement 57

CHAPTER **PAGE**

4.2.4 Step-4 : Design Flexibility for Other Azeotropic Systems 68

V CONCLUSIONS AND RECOMMENDATIONS 81

5.1 Conclusions 81

5.2 Recommendations 82

REFERENCES 83

APPENDICES

Appendix A Solubility Parameter (δ_{IL}) Values of Ionic Liquids 93

Appendix B Solubility of ILs and Target Component 98

Appendix C Thermodynamic and Physical Properties of Components Considered in PRO/II 109

Appendix D Azeotropic Separation Process Flowsheet and Stream Tables Implemented in PRO/II 116

CURRICULUM VITAE 186

LIST OF TABLES

TABLE		PAGE
2.1	Azeotropic data for binary mixtures	7
2.2	Group contribution values for ionic liquid Hildebrand solubility parameter model	14
2.3	Groups considered for the modified Lydersen–Joback–Reid method	16
2.4	Group Contributions for Parameters A, B, and D	19
2.5	Ionic liquids used as azeotrope breakers on literature for the separating of water + ethanol, ethanol/water relative volatility from VLE data (α^{VLE}) at azeotropic composition	28
2.6	Lists the ILs used as azeotrope breakers for the (water + other alcohols) longer than ethanol binary systems	33
2.7	Lists the ionic liquids used as azeotrope breakers for the (THF + water) system in the literature for extractive distillation	37
4.1	Extended GC values for ILs Hildebrand solubility parameter model	47
4.2	Four best IL candidates for the aqueous systems (Step 2)	53
4.3	Two best IL candidates for the non-aqueous systems (Step 2)	54
4.4	Separation task for ILs -based extractive distillation process	61
4.5	The degradation temperature of four best IL candidates	61
4.6	Input variables and the simulation results for ILs-based separation of the ethanol and water	63
4.7	A comparison of the input variables and the simulation results for alcoholic aqueous azeotropic separation processes using $[C_2MIM][N(CN)_2]$ when fixed condition as ethanol + water separation (Figure 4.8)	72

LIST OF TABLES

TABLE		PAGE
4.8	The input variables and the theoretical stages results for isopropanol + water separation processes using $[C_2MIM][N(CN)_2]$ when kept reflux ration as 0.729	75
4.9	A comparison of the input variables and the theoretical stages results for isopropanol + water separation processes using $[C_2MIM][N(CN)_2]$ when kept reflux ration as 0.729	76
4.10	A comparison of the input variables and the theoretical stages results for isopropanol + water separation processes using $[C_2MIM][N(CN)_2]$	78
A1	The experimental and predicted solubility parameter (δ_{IL}) values of ionic liquids	94
B1	The mole fraction solubility of the ILs in water at 298.15 K	100
B2	The mole fraction solubility of ILs in benzene at 298.15 K	105
C1	Properties of selected ionic liquids	109
C2	Heat of vaporization parameter for Ethanol, Water, and EG	110
C3	NRTL interaction parameters for the ternary system ethanol + water + EG	110
C4	NRTL interaction parameters for the ternary system ethanol + water + $[C_2mim][EtSO4]$	110
C5	NRTL interaction parameters for the ternary system ethanol + water + $[C_1mim][DMP]$	111
C6	NRTL interaction parameters for the ternary system ethanol + water + $[C_2mim][Ac]$	111

LIST OF TABLES

TABLE		PAGE
C7	NRTL interaction parameters for the ternary system ethanol + water + $[C_2mim][N(CN)_2]$	111
C8	NRTL interaction parameters for the ternary system isopropanol + Water + $[C_1mim][DMP]$	112
C9	NRTL interaction parameters for the ternary system isopropanol + Water + $[C_2mim][N(CN)_2]$	112
D1	Extractive distillation column properties using ethylene glycol (EG)	117
D2	Pump properties of the separation process	117
D3	Heat exchanger properties of the separation process	117
D4	Stream table of the conventional extractive distillation process using ethylene glycol (EG)	118
D5	Extractive distillation column properties using $[C_2mim][EtSO_4]$	126
D6	Flash properties of the separation process using $[C_2mim][EtSO_4]$	126
D7	Pump properties of the separation process using $[C_2mim][EtSO_4]$	126
D8	Stream table of the extractive distillation process using $[C_2mim][EtSO_4]$	128
D9	Extractive distillation column properties using $[C_1mim][DMP]$	134
D10	Flash properties of the separation process using $[C_1mim][DMP]$	134
D11	Pump properties of the separation process using $[C_1mim][DMP]$	134

LIST OF TABLES

TABLE		PAGE
D12	Stream table of the extractive distillation process using $[C_1mim][DMP]$	136
D13	Extractive distillation column properties using $[C_2mim][Ac]$	142
D14	Stream table of the extractive distillation process using $[C_2mim][Ac]$	143
D15	Extractive distillation column properties using $[C_2mim][N(CN)_2]$	148
D16	Flash properties of the separation process using $[C_2mim][N(CN)_2]$	148
D17	Pump properties of the separation process using $[C_2mim][N(CN)_2]$	148
D18	Stream table of the extractive distillation process using $[C_2mim][N(CN)_2]$	150
D19	Optimal extractive distillation column properties using [C1mim][DMP]	156
D20	Flash properties of the optimal separation process using $[C_1mim][DMP]$	156
D21	Pump properties of the optimal separation process using $[C_1mim][DMP]$	156
D22	Stream table of the optimal extractive distillation process using $[C_1mim][DMP]$	157
D23	Extractive distillation column properties using $[C_1mim][DMP]$	163
D24	Stream table of the extractive distillation process using $[C_1mim][DMP]$	164

LIST OF TABLES

TABLE		PAGE
D25	Extractive distillation column properties using $[C_2mim][N(CN)_2]$	169
D26	Flash properties of the separation process using $[C_2mim][N(CN)_2]$	169
D27	Pump properties of the separation process using $[C_2mim][N(CN)_2]$	169
D28	Stream table of the extractive distillation process using $[C_2mim][N(CN)_2]$	171
D29	Extractive distillation column properties using $[C_2mim][N(CN)_2]$	176
D30	Flash properties of the separation process using $[C_2mim][N(CN)_2]$	177
D31	Pump properties of the separation process using $[C_2mim][N(CN)_2]$	177
D32	Stream table of the extractive distillation process using $[C_2mim][N(CN)_2]$	178
D33	Optimal extractive distillation column properties using $[C_2mim][N(CN)_2]$	180
D34	Flash properties of the optimal separation process using $[C_2mim][N(CN)_2]$	180
D35	Pump properties of the optimal separation process using $[C_2mim][N(CN)_2]$	180
D36	Stream table of the optimal extractive distillation process using $[C_2mim][N(CN)_2]$	181

ต้นฉบับ หน้าขาดหาย

LIST OF FIGURES

FIGURE		PAGE
2.11	Acetate/alcohol relative volatility versus IL (Orchillés *et al.*, 2007, Vercher *et al.*, 2007, Li *et al.*, 2009) used for (ethanol+ ethyl acetate) system at azeotropic composition ($x_{Ethyl\ acetate} \approx 0.54$) and $x_{IL} \approx 0.30$.	40
2.12	Relative volatilities for the system 1-hexene (80 wt %)/n-hexane (20 wt %) using ILs at 303.15 K.	42
4.1	Comparison between experimental and predicted solubility parameter values.	47
4.2	Overall methodology for the screening of ILs and for the design of ILs-based separation processes.	50
4.3	Summary of the miscibility between ILs and target component screening concept (step 2).	51
4.4	Solubility of ILs in water expressed as a function of the solubility parameters of the ILs.	55
4.5	Solubility of ILs in benzene expressed as a function of the solubility parameters of the ILs.	56
4.6	Conventional extractive distillation process using ethylene glycol (EG).	58
4.7	The process diagram of ILs-based azeotropic separation process.	60
4.8	The optimal conditions and the results of the ethanol + water azeotropic separation processes using $[C_1MIM][DMP]$.	65
4.9	Energy requirement for reboiler in extractive distillation process using EG and four best IL candidates.	66
4.10	Overall energy requirement for extractive distillation process using EG and ILs.	67

LIST OF FIGURES

FIGURE		PAGE
4.11	Extractive distillation column of isopropanol + water separation using [C_1MIM][DMP].	69
4.12	VLE diagram of ethanol/water /[C_1MIM][DMP] (a) and VLE diagram of isopropanol/water /[C_1MIM][DMP] (b) at [C_1MIM][DMP] 20%mol (P = 1 atm).	70
4.13	The process flow diagram of isopropanol + water azeotropic separation using [C_2MIM][$N(CN)_2$].	71
4.14	Heat requirement for the alcoholic + water azeotropic separation using [C_2MIM][$N(CN)_2$] as entrainer.	73
4.15	Comparison of the number of theoretical stage versus liquid molar fraction of the product (isopropanol) in extractive distillation using [C_2MIM][$N(CN)_2$].	74
4.16	Comparison of the flowrate of [C_2MIM][$N(CN)_2$] versus liquid molar fraction of the isopropanol in EDC.	77
4.17	A comparison of the flash simulation results for the alcoholic aqueous azeotropic separation processes using [C_2MIM][$N(CN)_2$].	79
4.18	A comparison of the flash simulation results for the alcoholic aqueous azeotropic separation processes using [C_2MIM][$N(CN)_2$].	79
4.19	The optimal conditions and the results of the isopropanol + water azeotropic separation processes using [C_2MIM][$N(CN)_2$].	80
C1	VLE diagram of ethanol + water + [C_2mim][$EtSO_4$] at different concentration of ILs (using ICAS) at T = 300 K and P = 1 atm.	113

LIST OF FIGURES

FIGURE		PAGE
C2	VLE diagram of ethanol + water + [C_1mim][DMP] at different concentration of ILs (using ICAS) at T = 300 K and P = 1 atm.	113
C3	VLE diagram of ethanol + water + [C_2mim][Ac] at different concentration of ILs (using ICAS) at T = 300 K and P = 1 atm.	114
C4	VLE diagram of ethanol + water + [C_2mim][$N(CN)_2$] at different concentration of ILs (using ICAS) at T = 300 K and P = 1 atm.	114
C5	VLE diagram of isopropanol + water + [C_1MIM][DMP] at different concentration of ILs (using ICAS) at T = 300 K and P = 1 atm.	115
C6	VLE diagram of isopropanol + water + [C_2MIM][$N(CN)_2$] at different concentration of ILs (using ICAS) at T = 300 K and P = 1 atm.	115
D1	Conventional extractive distillation process flowsheet using ethylene glycol (EG).	116
D2	Overview of temperature and flowrate of the extractive distillation process (column T1) using [EG] vs. tray number.	120
D3	Overview of liquid fraction of the components in the extractive distillation process (column T1) using [EG] vs. tray number.	121
D4	Separation factor in the extractive distillation process (column T1) using [EG] vs. tray number.	122

LIST OF FIGURES

FIGURE		PAGE
D5	Overview of temperature and flowrate of the recovery process (column T2) using [EG] vs. tray number.	123
D6	Liquid fraction of EG the recovery process (column T2) using [EG] vs. tray number.	124
D7	Extractive distillation process flowsheet using [C_2mim][$EtSO_4$].	125
D8	Reboiler heat duty and overall heat duty as a function of feed stage location for separation of the ethanol + water azeotrope using [C_2mim][$EtSO_4$] = 85.07 kg-mol/hr (fixed Ns = 30 stages).	127
D9	Overview of temperature and flowrate of the extractive distillation process (column T1) using [C_2mim][$EtSO_4$] vs. tray number.	129
D10	Overview of liquid fraction of the components in the extractive distillation process (column T1) using [C_2mim][$EtSO_4$] vs. tray number.	130
D11	Separation factor in the extractive distillation process (column T1) using [C_2mim][$EtSO_4$] vs. tray number.	131
D12	Overview of temperature and flowrate in the stripping column (column T2) using [C_2mim][$EtSO_4$] vs. tray number.	132
D13	Extractive distillation process flowsheet using [C_1mim][DMP].	133
D14	Reboiler heat duty and overall heat duty as a function of feed stage location for separation of the ethanol + water azeotrope using [C_1mim][DMP] = 53.48 kg-mol/hr (fixed Ns = 30 stages).	135

LIST OF FIGURES

FIGURE		PAGE
D15	Overview of temperature and flowrate of the extractive distillation process (column T1) using [C_1mim][DMP] vs. tray number.	137
D16	Overview of liquid fraction of the components in the extractive distillation process (column T1) using [C_1mim][DMP] vs. tray number.	138
D17	Separation factor in the extractive distillation process (column T1) using [C_2mim][$EtSO_4$] vs. tray number.	139
D18	Overview of temperature and flowrate in the stripping column (column T2) using [C_1mim][DMP] vs. tray number.	140
D19	Extractive distillation process flowsheet using [C_2mim][Ac].	141
D20	Reboiler heat duty and overall heat duty as a function of feed stage location for separation of the ethanol + water azeotrope using [C_2mim][Ac] = 48.50 kg-mol/hr (fixed Ns = 30 stages).	142
D21	Overview of temperature and flowrate of the extractive distillation process (column T1) using [C_2mim][Ac] vs. tray number.	144
D22	Overview of liquid fraction of the components in the extractive distillation process (column T1) using [C_2mim][Ac] vs. tray number.	145
D23	Separation factor in the extractive distillation process (column T1) using [C_2mim][Ac] vs. tray number.	146
D24	Extractive distillation process flowsheet using [C_2mim][$N(CN)_2$].	147

LIST OF FIGURES

FIGURE		PAGE
D25	Reboiler heat duty and overall heat duty as a function of feed stage location for separation of the ethanol + water azeotrope using [C_2mim][$N(CN)_2$]= 120 kg-mol/hr (fixed Ns=30 stages).	149
D26	Overview of temperature and flowrate of the extractive distillation process (column T1) using [C_2mim][$N(CN)_2$] vs. tray number.	151
D27	Overview of liquid fraction of the components in the extractive distillation process (column T1) using [C_2mim][$N(CN)_2$] vs. tray number.	152
D28	Separation factor in the extractive distillation process (column T1) using [C_2mim][$N(CN)_2$] vs. tray number.	153
D29	Overview of temperature and flowrate in the stripping column (column T2) using [C_2mim][$N(CN)_2$] vs. tray number.	154
D30	Extractive distillation process flowsheet using [C_1mim][DMP].	155
D31	Overview of temperature and flowrate of the optimal extractive distillation process (column T1) using [C_1mim][DMP] vs. tray number.	158
D32	Overview of temperature and flowrate of the optimal extractive distillation process (column T1) using [C_1mim][DMP] vs. tray number.	159
D33	Separation factor in the optimal extractive distillation process (column T1) using [C_1mim][DMP] vs. tray number.	160

LIST OF FIGURES

FIGURE		PAGE
D34	Overview of temperature and flowrate in the optimal stripping column (column T2) using [C_1mim][DMP] vs. tray number.	161
D35	Extractive distillation process flowsheet using [C_1mim][DMP].	162
D36	Overview of temperature and flowrate of the extractive distillation process (column T1) using [C_1mim][DMP] vs. tray number.	165
D37	Overview of liquid fraction of the components in the extractive distillation process (column T1) using [C_1mim][DMP] vs. tray number.	166
D38	Separation factor in the extractive distillation process (column T1) using [C_1mim][DMP] vs. tray number	167
D39	Extractive distillation process flowsheet using [C_2mim][$N(CN)_2$].	168
D40	Reboiler heat duty and overall heat duty as a function of feed stage location for separation of the ethanol + water azeotrope using [C_2mim][$N(CN)_2$]= 120 kg-mol/hr (fixed Ns=30 stages, Nf = 20).	170
D41	Overview of temperature and flowrate of the extractive distillation process (column T1) using [C_2mim][$N(CN)_2$] vs. tray number.	172
D42	Overview of liquid fraction of the components in the extractive distillation process (column T1) using [C_2mim][$N(CN)_2$] vs. tray number.	173
D43	Separation factor in the extractive distillation process (column T1) using [C_2mim][$N(CN)_2$] vs. tray number.	174

LIST OF FIGURES

FIGURE		PAGE
D44	Overview of temperature and flowrate in the stripping column (column T2) using $[C_2mim][N(CN)_2]$ vs. tray number.	175
D45	Extractive distillation process flowsheet using $[C_2mim][N(CN)_2]$.	176
D46	Comparison of the flowrate of $[C_2MIM][N(CN)_2]$ versus liquid molar fraction of the ethanol in EDC.	177
D47	Extractive distillation process flowsheet using $[C_2mim][N(CN)_2]$.	179
D48	Overview of temperature and flowrate of the extractive distillation process (column T1) using $[C_2mim][N(CN)_2]$ vs. tray number.	182
D49	Overview of liquid fraction of the components in the extractive distillation process (column T1) using $[C_2mim][N(CN)_2]$ vs. tray number.	183
D50	Separation factor in the extractive distillation process (column T1) using $[C_2mim][N(CN)_2]$ vs. tray number.	184
D51	Overview of temperature and flowrate in the stripping column (column T2) using $[C_2mim][N(CN)_2]$ vs. tray number.	185

ABBREVIATIONS

Nomenclature of the Ionic Liquids

Cations

$[MIM]^+$	N-methylimidazolium
$[MMIM]^+$	1-Methyl-3-methylimidazolium
$[EMIM]^+$	1-Ethyl-3-methylimidazolium
$[PMIM]^+$	1-Propyl-3-methylimidazolium
$[BMIM]^+$ or $[C4\text{-}MIM]^+$	1-Butyl-3-methylimidazolium
$[HMIM]^+$ or $[C6\text{-}MIM]^+$	1-Hexyl-3-methylimidazolium
$[OMIM]^+$	1-Methyl-3-octylimidazolium
$[DMIM]^+$	1-Decyl-3-methylimidazolium
$[DoMIM]^+$	1-Dodecyl-3-methylimidazolium
$[EEIM]^+$	1-Ethyl-3-ethylimidazolium
$[AMIM]^+$	1-Allyl-3-methylimidazolium
$[EMMIM]^+$	1-Ethyl-2,3-dimethylimidazolium
$[(EtOH)MIM]^+$	1-(2-Hydroxyethyl)-3-methyl-imidazolium
$[(EtOH)MMIM]^+$	1-(2-Hydroxyethyl)-2,3-dimethylimidazolium
$[(HeOH)MIM]^+$	1-(6-Hydroxyhexyl)-3-methylimidazolium
$[Epy]^+$	1-Ethylpyridinium
$[EMpy]^+$	1-Ethyl-3-methylpyridinium
$[3MBpy]^+$	3-Methyl-N-butylpyridinium
$[4MBpy]^+$	4-Methyl-N-butylpyridinium
$[C6\text{-}PY]^+$	1-hexylpyridinium
$[OMpy]^+$	1-Octyl-4-methylpyridinium
$[BMpyr]^+$	1-Butyl-1-methylpyrrolidinium
$[P_{6\,6\,6\,14}]^+$ or $[3C6\text{-}C14\text{-}Ph]^+$	Trihexyl(tetradecyl)phosphonium
$[EEES]^+$	Triethylsulfonium
$[MOOON]^+$ or $[C1\text{-}3C8\text{-}Am]^+$	Methyltrioctylammonium
$[(EtOH)NH_3]^+$	Monoethanolammonium

$[(EtOH)_2NH_2]^+$	Diethanolammonium
$[(EtOH)_3NH]^+$	Triethanolammonium
$[MMM(EtOH)N]^+$	(2-Hydroxyethyl)trimethylammonium
$[EMM(EtOH)N]^+$	Ethyl(2-hydroxyethyl)dimethylammonium
$[HMM(EtOH)N]^+$	Hexyl(2-hydroxyethyl)dimethylammonium
$[EEM(MeOEt)N]^+$	Diethylmethyl(2-methoxyethyl)ammonium
$[C6\text{-}C1\text{-}PYR]^+$	hexylmethylpyrrolidonium
$[C6\text{-}C1\text{-}PIP]^+$	hexylmethylpiperidinium
$[C6\text{-}Qui]^+$	hexylquinolinium
$[C8Chin]^+$	1-octylquinolinium

Anions

$[Br]^-$	Bromide
$[Cl]^-$	Chloride
$[PF_6]^-$	Hexafluorophosphate
$[BF_4]^-$	Tetrafluoroborate
$[OTf]^-$	Trifluoromethanesulfonate or Triflate or Trifluoromethylsulfonate
$[NTf_2]^-$	Bis(trifluoromethylsulfonyl)imide
$[PF_3(C_2F_5)_3]^-$	Tris(pentafluoroethyl)trifluorophosphate
$[OAc]^-$	Acetate
$[CF_3CO_2]^-$	Trifluoroacetate
$[CF_3SO_3]^-$	Nitrate
$[Salicylate]^-$	Salicylate
$[TOS]^-$	Tosylate
$[SCN]^-$	Thiocyanate
$[N(CN)_2]^-$	Dicyanamide
$[C(CN)_3]^-$	Tricyanomethanide
$[B(CN)_4]^-$ or [TCB]	Tetracyanoborate
$[BOB]^-$	Bis[oxalato(2-)]-borate
$[EtSO_4]^-$	Ethyl sulfate

$[MeSO_4]^-$	Methyl sulfate
$[OcSO_4]^-$	Octyl sulfate
$[Me(EtO)_2SO_4]^-$	Diethylenglycol monomethyl ether sulfate or 2-(2-methoxyethoxy)ethylsulfate
$[HSO_4]^-$	Hydrogen sulfate
$[MeSO_3]^-$	Methanesulfonate
$[ToSO_3]^-$	p-Toluenesulfonate
$[(Bu)_2PO_4]^-$	Dibutylphosphate
$[DMP]^-$	Dimethylphosphate
$[(Et)_2PO_4]^-$	Diethylphosphate
$[MePO_3]^-$	Methylphosphonate
$[(Me_3Pe)_2PO_2]^-$	Phosphonium Bis(2,4,4-trimethylpentyl) phosphinate
$[BMA]^-$	bis(methylsulfonyl) amide
$[BMB]^-$	bis(malonato(2-))borate
$[BTI]^-$	bis(trifluoromethyl-sulfonyl) imide
$[BTA]^-$	bis(trifluoromethylsulfonyl)amid
$[MAcA]^-$	Methylsulfonyl acetamide

LIST OF SYMBOLS

a_{nm} = group interaction parameter between groups n and m

A_k = Van Der Waals volume of group k

c_{ii} = cohesive energy density

C_i = contribution of group i

C_{pL} = liquid heat capacity

D = largest driving force

D_s = relative position of side-draw driving force

D_x = relative position of largest driving force

D_y = size of largest driving force

F = flowrate

F_i = surface area/mole fraction of component i

F_{ij} = driving force for component i for property j

g_{ij} = energy parameter characteristic of the i-j interaction

Δg_{ij} = binary interaction parameter between component i and j

Δh_{vap} = enthalpy of vaporization

K_1 = K-factor for component 1

K_2 = K-factor for component 2

M = molecular mass

n_i = number of groups of type i

n_i = number of times that a group appears in the molecule

N = number of stages

Nf = feed stage location

P = presure

P_C = critical pressure

P_1^s = vapor pressures of component 1

P_2^s = vapor pressures of component 2

q_i = relative van der Waals volumes molecular surface areas of component i

Q_k = relative van der Waals surface areas of group k

r_i = relative van der Waals volume of component i

R_k = relative van der Waals volume of group k

R = gas constant

RR = reflux ratio

SF = scaling factor

T = absolute temperature

T_b = normal boiling temperature

T_c = critical temperature

T_R = reduced temperature

T_{bR} = reduced temperature at the normal boiling point

v_i = molar volume of component i

V_i = volume/mole fraction of component i

V_C = critical volume

V_k = van der Waals group volumes of group k

x_1 = mole fraction for component 1 in the liquid phase

x_2 = mole fraction for component 2 in the liquid phase

X_m = fraction of group m in the mixture

$x_{LK,D}$ = specification for the light key distillate mole fraction

$x_{HK,B}$ = specification for the heavy key bottoms mole fraction

y_1 = mole fraction for component 1 in the vapor phase

y_2 = mole fraction for component 2 in the vapor phase

Greek Symbols

α_{12} = separation factor or relative volatility

α_{ij} = non-randomness parameter in the NRTL equation

γ_1 = activity coefficient of component 1

γ_2 = activity coefficient of component 2

γ_i^C = caombination part of the activity coefficient of component i

γ_i^R = residual part of the activity coefficient of component i

β_{ij} = relative separability parameter for component i with respect to property j

Γ_k = group residual activity coefficient of group k

δ_i = solubility parameter of component i

ψ_{nm} = group interaction parameter

θ_m = surface area fractions

ω = acentric factor

ρ_L = liquid densities of the ionic liquids