

IONIC-LIQUID BASED SEPARATION OF AZEOTROPIC MIXTURES

Kusuma Kulajanpeng

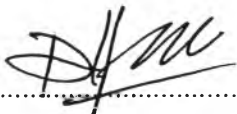
A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
The University of Michigan, The University of Oklahoma,
Case Western Reserve University, and Institut Français du Pétrole
2014

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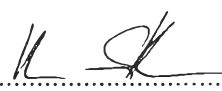
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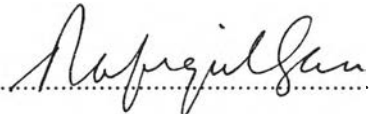
Thesis Title: Ionic-Liquid Based Separation of Azeotropic Mixtures
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Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

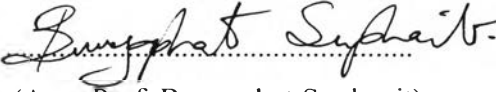

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ABSTRACT

5571006063: Petrochemical Technology Program

Kusuma Kulajanpeng: Ionic-Liquid Based Separation of Azeotropic Mixtures.

Thesis Advisors: Dr. Uthaiporn Suriyaphradilok and Prof. Rafiqul Gani 186 pp. -

Keywords: Ionic liquids/ Extractive distillation / Azeotropic mixture separation

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 กุละจันทรเพ็ง: การแยกของผสมอะซีโอโทรปด้วยของเหลวไอออนิก (Ionic-Liquid Based Separation of Azeotropic Mixtures) อ. ที่ปรึกษา: ดร. อุทัยพร สุริยประภาติลล และ ศ.ดร. ราฟีก กานี 186 หน้า

วิธีการสำหรับการคัดเลือกของเหลวไอออนิกเป็นสารช่วยกลั่น (entrainers) และการออกแบบกระบวนการแยกโดยใช้ของเหลวไอออนิกใช้ในหลากหลายระบบของผสมอะซีโอโทรปสององค์ประกอบที่เป็นเนื้อเดียวกันถูกนำเสนอในงานวิจัยนี้ ผ่านสองกรณีศึกษาคือเอทานอล + น้ำ และ ไอโซโพรพานอล + น้ำ ของเหลวไอออนิกถูกคัดเลือกจากหลักเกณฑ์ดังนี้คือความเสถียร ความเป็นพิษ ผลกระทบต่อสิ่งแวดล้อม การผสมเข้ากันได้กับน้ำและพารามิเตอร์การละลาย (Hildebrand solubility parameter group contribution) ของของเหลวไอออนิก จากการศึกษาพบว่าของเหลวไอออนิกที่ดีที่สุดสำหรับระบบที่ประกอบด้วยน้ำคือ 1-Ethyl-3-Methylimidazolium Ethylsulfate [C_2MIM][EtSO₄], 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 บนพื้นฐานของการใช้พลังงานน้อยที่สุดซึ่งสามารถลดพลังงานได้ถึง 22 % เมื่อเปรียบเทียบกับการใช้สารละลายโดยทั่วไป (Ethylene glycol) ความยืดหยุ่นในการออกแบบสำหรับกระบวนการแยกของผสมอะซีโอโทรปด้วยของเหลวไอออนิกตัวเดิมความบริสุทธิ์ของผลิตภัณฑ์และพารามิเตอร์ในการออกแบบเหมือนเดิมกับการแยกเอทานอล + น้ำ ถูกศึกษา สำหรับของผสมอะซีโอโทรป ไอโซโพรพานอล + น้ำ ผลการศึกษาแสดงให้เห็นว่า [C_1MIM][DMP] ไม่สามารถทำให้แอลกอฮอล์บริสุทธิ์ 99.8 % เนื่องจากจำนวนชั้นของหอกลิ้นที่ใช้มากเกินไป โดยการกำหนดพารามิเตอร์การออกแบบทั้งหมดให้เหมือนกับระบบที่ใช้ [C_2MIM][N(CN)₂] เป็นสารช่วยกลั่น พบว่าการเพิ่มขึ้นของจำนวนอะตอมของคาร์บอนในแอลกอฮอล์จากเอทานอลเป็นไอโซโพรพานอล ส่งผลให้พลังงานที่ใช้ทั้งหมดลดลงเพราะว่าไอโซโพรพานอลกับน้ำมีปฏิสัมพันธ์ระหว่างกันที่อ่อนกว่าเอทานอลกับน้ำ ดังนั้นการสกัดน้ำออกจากไอโซโพรพานอลจึงทำได้ง่ายกว่าการสกัดน้ำออกจากเอทานอล

ACKNOWLEDGEMENTS

This work would not have been possible without the assistance of the following individuals:

Initially I am indebted grateful to Dr. Uthaiporn Suriyapraphadilok, my advisor, for providing invaluable knowledge, creative comments, untouchable experience in classroom, and kind support throughout this research work.

I offer my sincerest gratitude to Prof. Rafiqul Gani for giving me the best opportunity of visiting Computer Aided Process Engineering Center (CAPEC), Technical University of Denmark. During I worked in Denmark, he provided invaluable knowledge, creative suggestions, and kind support throughout this research work.

I would like to thank Asst. Prof. Kitipat Siemanond and Asst. Prof. Bunyaphat Suphanit for being my thesis committee. Their suggestions and comments are very beneficial for me and this work.

This thesis work is funded by the Petroleum and Petrochemical College and the Center of Excellence on Petrochemical and Materials Technology, Thailand.

I greatly appreciate all PPC staffs and my friends who gave me support and encouragement.

Finally, I am deeply indebted to my family for their love, understanding, encouragement, and support for me at all time.

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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-MIM] ⁺	1-Butyl-3-methylimidazolium
[HMIM] ⁺ or [C6-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-PY] ⁺	1-hexylpyridinium
[OMpy] ⁺	1-Octyl-4-methylpyridinium
[BMpyr] ⁺	1-Butyl-1-methylpyrrolidinium
[P ₆₆₆₁₄] ⁺ or [3C6-C14-Ph] ⁺	Trihexyl(tetradecyl)phosphonium
[EEES] ⁺	Triethylsulfonium
[MOOON] ⁺ or [C1-3C8-Am] ⁺	Methyltrioctylammonium
[(EtOH)NH ₃] ⁺	Monoethanolammonium

$[(\text{EtOH})_2\text{NH}_2]^+$	Diethanolammonium
$[(\text{EtOH})_3\text{NH}]^+$	Triethanolammonium
$[\text{MMM}(\text{EtOH})\text{N}]^+$	(2-Hydroxyethyl)trimethylammonium
$[\text{EMM}(\text{EtOH})\text{N}]^+$	Ethyl(2-hydroxyethyl)dimethylammonium
$[\text{HMM}(\text{EtOH})\text{N}]^+$	Hexyl(2-hydroxyethyl)dimethylammonium
$[\text{EEM}(\text{MeOEt})\text{N}]^+$	Diethylmethyl(2-methoxyethyl)ammonium
$[\text{C6-C1-PYR}]^+$	hexylmethylpyrrolidonium
$[\text{C6-C1-PIP}]^+$	hexylmethylpiperidinium
$[\text{C6-Qui}]^+$	hexylquinolinium
$[\text{C8Chin}]^+$	1-octylquinolinium

Anions

$[\text{Br}]^-$	Bromide
$[\text{Cl}]^-$	Chloride
$[\text{PF}_6]^-$	Hexafluorophosphate
$[\text{BF}_4]^-$	Tetrafluoroborate
$[\text{OTf}]^-$	Trifluoromethanesulfonate or Triflate or Trifluoromethylsulfonate
$[\text{NTf}_2]^-$	Bis(trifluoromethylsulfonyl)imide
$[\text{PF}_3(\text{C}_2\text{F}_5)_3]^-$	Tris(pentafluoroethyl)trifluorophosphate
$[\text{OAc}]^-$	Acetate
$[\text{CF}_3\text{CO}_2]^-$	Trifluoroacetate
$[\text{CF}_3\text{SO}_3]^-$	Nitrate
$[\text{Salicylate}]^-$	Salicylate
$[\text{TOS}]^-$	Tosylate
$[\text{SCN}]^-$	Thiocyanate
$[\text{N}(\text{CN})_2]^-$	Dicyanamide
$[\text{C}(\text{CN})_3]^-$	Tricyanomethanide
$[\text{B}(\text{CN})_4]^-$ or $[\text{TCB}]$	Tetracyanoborate
$[\text{BOB}]^-$	Bis[oxalato(2-)]-borate
$[\text{EtSO}_4]^-$	Ethyl sulfatate

[MeSO ₄] ⁻	Methyl sulfate
[OcSO ₄] ⁻	Octyl sulfate
[Me(EtO) ₂ SO ₄] ⁻	Diethylglycol monomethyl ether sulfate or 2-(2-methoxyethoxy)ethylsulfate
[HSO ₄] ⁻	Hydrogen sulfate
[MeSO ₃] ⁻	Methanesulfonate
[ToSO ₃] ⁻	p-Toluenesulfonate
[(Bu) ₂ PO ₄] ⁻	Dibutylphosphate
[DMP] ⁻	Dimethylphosphate
[(Et) ₂ PO ₄] ⁻	Diethylphosphate
[MePO ₃] ⁻	Methylphosphonate
[(Me ₃ Pe) ₂ PO ₂] ⁻	Phosponium 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_{ij} = 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
 N_f = feed stage location
 P = pressure
 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 = combination 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