

**PERVAPORATION FOR BIOFUEL REFINING:
MULTICOMPONENT PERMEATION AND COUPLING
EFFECTS IN ACETONE-BUTANOL-ETHANOL
SOLUTIONS**

ABEER MUSHTAQ MUTTO



DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

FEBRUARY 2025

© Indian Institute of Technology Delhi (IITD), New Delhi, 2025

**PERVAPORATION FOR BIOFUEL REFINING:
MULTICOMPONENT PERMEATION AND COUPLING
EFFECTS IN ACETONE-BUTANOL-ETHANOL
SOLUTIONS**

by

ABEER MUSHTAQ MUTTO

Department of Chemical Engineering

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

FEBRUARY 2025

Dedicated to my loving family.

*To my parents and grandparents,
and to my brother and sister-in-law;*

Thank you for believing in me.

Declaration

This is to certify that the thesis titled “**Pervaporation for Biofuel Refining: Multi-component Permeation and Coupling Effects in Acetone-Butanol-Ethanol Solutions**” has been authored by me. It presents the research conducted by me under the supervision of **Dr. Sharad Kumar Gupta** and **Dr. Rajesh Khanna**. To the best of my knowledge, it is an original work, both in terms of research content and narrative, and has not been submitted elsewhere, in part or in full, for a degree. Further, due credit has been attributed to the relevant state-of-the-art and collaborations (if any) with appropriate citations and acknowledgements, in line with established norms and practices.

Abeer Mushtaq Mutto

February 2025

Entry Number:2017CHZ8248

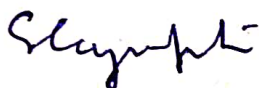
Department of Chemical Engineering

Indian Institute of Technology Delhi

Certificate

This is to certify that the thesis entitled "Pervaporation for Biofuel Refining: Multi-component Permeation and Coupling Effects in Acetone-Butanol-Ethanol Solutions", submitted by Abeer Mushtaq Mutto to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy, is a bonafide record of original research work carried out by her under our supervision in conformity with rules and regulations of the institute.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma to the best of our knowledge.

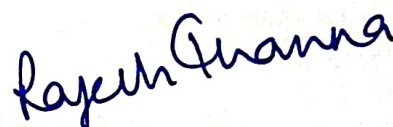


Dr Sharad Kumar Gupta

Professor

Department of Chemical Engineering

Indian Institute of Technology Delhi



Dr Rajesh Khanna

Professor

Department of Chemical Engineering

Indian Institute of Technology Delhi

Acknowledgements

“Fear wist not to evade, as Love wist to pursue”

-The Hound of Heaven, Francis Thompson

In the name of the Almighty, the most beneficent, the most merciful.

The production of this thesis has been a labor of love, and as with most arduous endeavors it would not have been possible without the collective kindness and generosity of the human spirit.

First of all, I would like to express my most ardent gratitude to Prof. Sharad Kumar Gupta, for guiding me through this experience. Words would fail me in expressing the amount of respect and inspiration Prof. Gupta invokes in me with the sharpness of his intellect, the discipline in his conduct and the grace of his character. True to his nature as an exemplary mentor, Prof Gupta has always precisely steered me towards the “broader picture” while simultaneously granting me enough freedom to explore my research independently. This thesis could not have been completed without his excellent scientific advice and motivation.

I would also like to extend my deepest gratitude to my co-supervisor Prof. Rajesh Khanna, for his constant support and keen interest in my research work. His expert advice has been invaluable to the completion of this work. His remarkable scientific acumen and insightful reflections on life beyond research, have provided both wisdom and encouragement throughout this journey.

I am also extremely thankful to my research committee members throughout these years: Prof. Anupam Shukla, Prof. Anil Verma, Prof. Sudip Pattanayek and Prof P.M.V Subbarao for their thoughtful suggestions and directions for my research work. A special acknowledgement is also reserved for the entire faculty, staff and peers at the Department of Chemical Engineering, IIT Delhi, without whose constant encouragement and assistance this endeavor would not have been possible. I am especially indebted to lab members and seniors at the Membrane Engineering Lab; Mr. Ketan Mahawer, Mr. Vivek Srivastava, Mr. Sachin Thorat, Dr. Manish Jain and Dr. Dinesh Attarde for their unwavering help and support.

To my dear friends, Dr Komal Tripathi, Ms. Rumysa Manzoor, and Dr. Suaiba Mufti, I extend my warmest thanks. Thank you for lending a reassuring ear to the often oddly timed tales of my adventures. I am also immensely appreciative of my roommate, Ms.

Kartiki, for her heartwarming meals and the many ‘sisters’ I met throughout these years for their care and kindness.

Foremost and most importantly, I could never be too appreciative of my beloved family, both immediate and extended for the unconditional love and blessings they have given me. To my ever-supportive father, Mr Mushtaq Ahmed Mutto, and my brave mother , Mrs. Arjmand Shaheen, Thank-you feels embarrassingly inadequate to convey my gratitude for everything you have done for me. Your nurturing of my curious eccentricities has made me the person I am today. To my dearest Nani, thank you for your innocent prayers and the “pocket money” you still send my way as a token of your love. To the most generous of brothers, Umi bhaya, it took standing on your shoulders for me to even dare take flight. And to Hudda, thank you for filling my days with so much love and giving me a wonderfully joyous surprise just a day before I submitted this thesis – my precious niece, Duha. I also thank my dear cousins for being there to vent to and my dearest aunts for their abundant love and blessings.

And at last, I would like to conclude as I began, by offering a humble exaltation to the Almighty. Today I find myself transformed into a completely different person from when I started this Ph.D., and I am grateful to Almighty Allah for granting me strength, resilience and hope throughout this transcendent experience. As they say, it truly takes a village; and I am thankful for the wonderful innumerable others Allah placed in my path.

(Abeer Mushtaq Mutto)

*that which we are, we are;
One equal temper of heroic hearts,
Made weak by time and fate,
but strong in will
To strive, to seek, to find,
and not to yield.*

*Ulysses,
Alfred Lord Tennyson*

Abstract

The nascent field of biofuels derived from renewable lignocellulosic resources offers a promising solution to the finite supply of fossil fuels and the ensuing climatic, economic and political challenges. However, aspirations of large scale and scalable biorefining of bio-butanol from multicomponent Acetone-Butanol-Ethanol (ABE) fermentation broths through organophilic pervaporation are still challenged, in part, by a limited knowledge on the effect of by-products ethanol and acetone on final recovery. This study, therefore, involves experimental investigations on multicomponent permeation in pervaporation followed by the modeling and quantification of the impact of coupling phenomena on the selective transport of butanol via a diverse portfolio of semi-empirical, statistical, and theoretical frameworks. Equilibrium sorption, pure and mixture permeation experiments were conducted using a commercial polydimethylsiloxane (PDMS) membrane (PERVAP-4060) with individual solvent content $\leq 6wt.\%$ over a temperature range of 303.15–323.15 K, relevant to fermentation processes.

Initially, modified solution-diffusion models are customized to emulate temperature and concentration dependence of permeation in binary and ternary feed mixtures. After initial screening of thermodynamic models and simulation of activity coefficients and volume fractions, a rationally designed experimental and statistically validated empirical investigation of sorption characteristics and the influence of coupling on fluxes in quaternary ABE mixtures using sorption and flux isotherms is followed. Finally, Maxwell-Stefan (MS) diffusion formulations, combined with the UNIQUAC thermodynamic model, are extended to multicomponent ABE feed solutions to resolve coupling into its thermodynamic and kinetic (diffusive) constituents. A generalized and explicit analytical derivation for calculation of

thermodynamic correction factors by UNIQUAC model is proposed, allowing estimation for any number of permeants.

The membrane is observed to be most intrinsically selective towards butanol in all systems and compositions. However, coupling effects were observed to limit permeation, especially at higher solvent concentrations. Analysis of phenomenological parameters reveal that while the additional plasticization by other penetrants benefit butanol permeation, their presence also induced a reduction in the free volume expansion by butanol itself. Furthermore, though sorption isotherms reveal that butanol volume fractions in the membrane remain unaffected by feed composition, flux isotherms also reaffirm that the positive coupling due to additional plasticization decreases at higher solvent concentrations, suggesting other physical associations or cluster formation between penetrants to be the causative factor. Subsequently, a detailed hit-and-trial based strategy is implemented to evaluate the relevance of membrane plasticization, cluster formation and interspecies frictional interactions on effective diffusivities. The optimal model fit is found to be insensitive to variation in MS cross-diffusivities, affirming the trivial contribution of correlation effects between penetrants, provided the expressions for self-diffusivities are adequately tailored for membrane plasticization and clustering. Notably, while only butanol clustering suffices for binary mixtures, additional aggregates involving butanol-water, water-water, and butanol-acetone/ethanol are suggested to play a crucial role in steering diffusivities in ternary solutions.

Overall, by a careful manipulation of solvent ratios – for instance at lower butanol to second component ratios in feed; multicomponent coupling effects were demonstrated to significantly enhance butanol permeances through the polymeric membranes, achieving nearly twice the values observed in binary systems. In contrast, minimal coupling is experienced

at equimolar conditions, allowing multicomponent pervaporation to be satisfactorily modeled as binary separation in such limiting cases. Additionally, the modelling of quaternary ABE fermentation solutions was also simplified to ternary mixtures by showing that mutual interactions between acetone and ethanol have minimal impact on butanol transport utilizing Response Surface Methodology based statistical analysis. Furthermore, a deeper understanding of the physico-chemical origins of coupling effects was achieved, particularly the synergy between membrane plasticization and kinetic coupling mechanisms. These insights can guide the development of superior energy-efficient membrane materials with improved diffusivity and sorption selectivities by optimizing the free-volume-diffusivity paradigms for enhanced targeted recovery from complex industrial feed mixtures.

सारांश

पेट्रोलियम ईंधन की सीमित आपूर्ति और इससे जुड़ी जलवायु, आर्थिक और राजनीतिक चुनौतियों के समाधान के लिए, नवीकरणीय लिग्नोसेल्यूलोसिक संसाधनों से प्राप्त जैव-ईंधन एक आशाजनक विकल्प के रूप में उभर रहा है। हालांकि, बहु-घटक एसीटोन-ब्यूटानॉल-इथेनॉल (ABE) किण्वन मिश्रण से जैव-ब्यूटानॉल के बड़े पैमाने पर और स्केलेबल जैव-रिफाइनिंग को ऑर्गनोफिलिक मेम्ब्रेन पर्मेपोरेशन के माध्यम से प्राप्त करने की महत्वाकांक्षा अभी भी चुनौतियों का सामना कर रही है, जिसमें आंशिक रूप से सह-उत्पाद इथेनॉल और एसीटोन के अंतिम पुनर्प्राप्ति पर प्रभाव के बारे में सीमित जानकारी है। इस अध्ययन में, पर्मेपोरेशन में बहु-घटक पारगमन पर प्रयोगात्मक जांच और अर्ध-अनुभवजन्य, सांख्यिकीय और सैद्धांतिक ढांचों के विविध संग्रह के माध्यम से युग्मन (coupling) घटनाओं के चयनात्मक ब्यूटानॉल परिवहन पर प्रभाव के प्रतिरूपण और परिमाणन को शामिल किया गया है। शुद्ध और मिश्रण सॉर्प्शन और फ्लक्स प्रयोगों को वाणिज्यिक पॉलीडाइमिथाइलसिलोक्सेन (PDMS) मेम्ब्रेन (PERVAP-4060) का उपयोग करके 303.15–323.15 K के तापमान पर और ≤ 6 वज़न प्रतिशत विलायक सामग्री के साथ किया गया।

शुरुआत में, संशोधित सॉल्यूशन-डिफ्यूजन (solution-diffusion) मॉडल को बाइनरी और टर्नरी फीड मिश्रणों में पारगम्यता के तापमान और सांद्रता पर निर्भरता को प्रदर्शित करने के लिए अनुकूलित किया गया। थर्मोडायनामिक मॉडल्स की प्रारंभिक जांच और एक्टिविटी गुणांक तथा वॉल्यूम फ्रैक्शन का अनुकरण करने के बाद, एक तार्किक रूप से डिज़ाइन किया गया प्रयोगात्मक और सांख्यिकीय रूप से मान्य अनुभवजन्य अध्ययन किया गया, जिसमें सोखने की विशेषताओं और चतुर्धातुक ABE मिश्रणों में फ्लक्स पर युग्मन के प्रभाव को सोखने और फ्लक्स आइसोथर्म (के माध्यम से परखा गया। अंततः, मैक्सवेल-स्टेफन (Maxwell-Stefan) डिफ्यूजन सूत्रों को UNIQUAC थर्मोडायनामिक मॉडल के साथ मिलाकर बहु-घटक ABE फीड समाधानों में विस्तारित किया गया, जिससे युग्मन को थर्मोडायनामिक और गतिज (kinetic) घटकों में विभाजित किया जा सके। UNIQUAC मॉडल द्वारा थर्मोडायनामिक करेक्शन फैक्टर की गणना के लिए एक सामान्य और स्पष्ट विश्लेषणात्मक व्युत्पत्ति प्रस्तावित की गई, जो किसी भी संख्या के विलायक का अनुमान लगाने की अनुमति देती है।

मेम्ब्रेन को सभी प्रणालियों और संघटनों में ब्यूटानॉल के प्रति सबसे अधिक आंतरिक रूप से चयनात्मक पाया गया। हालांकि, युग्मन प्रभाव ने विशेष रूप से उच्च सॉल्वेंट सांद्रता पर पारगम्यता को सीमित कर दिया। प्रकट परिघटनात्मक मानकों के विश्लेषण से पता चला कि अन्य प्रवेशकों द्वारा अतिरिक्त प्लास्टिसाइजेशन ने ब्यूटानॉल पारगम्यता को लाभ पहुंचाया, लेकिन उनकी उपस्थिति ने ब्यूटानॉल द्वारा मुक्त आयतन (free volume) के विस्तार को भी कम कर दिया। इसके अलावा, यद्यपि सोखने की आइसोथर्म यह दर्शाती हैं कि मेम्ब्रेन में ब्यूटानॉल का आयतन अंश फीड संघटन से अप्रभावित रहता है, फ्लक्स आइसोथर्म भी यह पुनः पुष्टि करती हैं कि अतिरिक्त प्लास्टिसाइजेशन के कारण सकारात्मक युग्मन उच्च सॉल्वेंट सांद्रता पर घट जाता है, जो प्रवेशकों के बीच अन्य भौतिक संघों या क्लस्टर निर्माण को इसका संभावित कारण बताता है। इसके बाद, प्रभावी विसरणशीलता पर मेम्ब्रेन प्लास्टिसाइजेशन, क्लस्टर निर्माण और प्रजातियों के बीच घर्षणीय अंतःक्रियाओं की प्रासंगिकता का मूल्यांकन करने के लिए एक विस्तृत हिट-एंड-ट्रायल रणनीति लागू की गई। आदर्श मॉडल फिट को MS क्रॉस-डिफ्यूजिविटी में बदलाव के प्रति असंवेदनशील पाया गया, यह पुष्टि करते हुए कि प्रवेशकों के बीच सहसंबंधीय प्रभाव का योगदान नगण्य है, बशर्ते कि आत्म-विसरणशीलता के लिए अभिव्यक्तियों को मेम्ब्रेन प्लास्टिसाइजेशन और क्लस्टरिंग के लिए ठीक से तैयार किया गया हो। विशेष रूप से, जबकि केवल ब्यूटानॉल क्लस्टरिंग बाइनरी मिश्रणों के लिए पर्याप्त है, ब्यूटानॉल-पानी, पानी-पानी, और ब्यूटानॉल-एसीटोन/एथेनॉल को शामिल करने वाले अतिरिक्त समुच्चय टर्नरी समाधान में विसरणशीलता को नियंत्रित करने में महत्वपूर्ण भूमिका निभाते हैं।

कुल मिलाकर, सॉल्वेंट अनुपात में सावधानीपूर्वक हेरफेर द्वारा — जैसे कि फीड में ब्यूटानॉल और दूसरे घटक के कम अनुपात पर — बहु-घटक युग्मन प्रभावों ने पॉलीमरिक मेम्ब्रेन के माध्यम से ब्यूटानॉल की पारगम्यता को उल्लेखनीय रूप से बढ़ाया, जिससे बाइनरी सिस्टम की तुलना में लगभग दो गुना अधिक मूल्य प्राप्त हुआ। इसके विपरीत, सममोलर स्थितियों में न्यूनतम युग्मन देखा गया, जिससे ऐसे सीमित मामलों में बहु-घटक परवपरेषन को बाइनरी पृथक्करण के रूप में संतोषजनक ढंग से मॉडल किया जा सका। इसके अतिरिक्त, क्वाटरनरी ABE किण्वन समाधान का मॉडलिंग टर्नरी मिश्रणों तक सरलीकृत किया गया, यह दर्शाते हुए कि एसीटोन और एथेनॉल के बीच पारस्परिक अंतःक्रियाओं का ब्यूटानॉल परिवहन पर न्यूनतम प्रभाव पड़ता है। इस सरलीकरण के लिए प्रतिक्रिया सतह पद्धति (Response Surface Methodology) आधारित सांख्यिकीय विश्लेषण का उपयोग किया गया। इसके अलावा, युग्मन प्रभावों की भौतिक-रासायनिक उत्पत्ति की एक गहन समझ प्राप्त की गई, विशेष रूप से मेम्ब्रेन प्लास्टिसाइजेशन और

गतिज युग्मन तंत्र के बीच तालमेल पर। इन जानकारीयों से अधिक ऊर्जा-कुशल मेम्ब्रेन के विकास में मार्गदर्शन मिल सकता है, जिनमें प्रसारशीलता और सोखने की चयनात्मकता में सुधार किया जा सकता है, ताकि जटिल औद्योगिक फीड मिश्रणों से लक्षित पुनर्प्राप्ति को बढ़ावा दिया जा सके।

Contents

Acknowledgements	iv
Abstract	vii
List of Figures	xvii
List of Tables	xxii
Abbreviations	xxv
Symbols	xxvi
Subscripts	xxix
Superscripts	xxx
Outline of Thesis	xxxi
1 Introduction	1
1.1 Background of the study: Opportunities and Obstacles in Biorefining of Acetone-Butanol-Ethanol Biofuels	1
1.2 Basics of Pervaporation	4
1.2.1 Transmembrane mass transport in pervaporation	7
1.2.2 Multicomponent permeation and coupling phenomena for pervaporation	8
1.3 Summary	10
2 Literature Review	12
2.1 Introduction	12
2.2 Review of Studies on Pervaporation of ABE Solutions and Other Multicomponent Mixtures in General	13
2.3 Choice of Organophilic Membrane for Pervaporation of ABE Solutions . . .	16
2.4 Modeling Multicomponent Permeation and Coupling Phenomena in Pervaporation	17

2.4.1	Overview of transmembrane Solution Diffusion model for pervaporation	20
2.4.2	Overview of modelling approaches describing sorption in pervaporation	21
2.4.3	Overview of modeling approaches used to describe multicomponent diffusion in pervaporation	24
2.5	Gaps in Literature and Motivation for Research	29
2.6	Objectives and Scope of the Thesis	31
3	Methodology	33
3.1	Introduction	33
3.2	Materials	33
3.3	Experimental Setup and Procedure	34
3.3.1	Equilibrium sorption tests	34
3.3.2	Permeation tests	36
3.3.3	Analytical techniques	38
3.3.4	Membrane performance evaluators	38
3.3.5	Design of experiments	39
3.4	Methodology for Parameter Estimation and Model Solution	43
4	Permeation in Binary and Ternary ABE Mixtures: Influence of Ethanol and Acetone on Butanol Transport using Modified Solution Diffusion Models	47
4.1	Introduction	47
4.2	Model Development	49
4.2.1	Solution Diffusion mass transport model for pervaporation	49
4.2.2	Modeling and coupling in ternary feed	53
4.3	Results and Discussions	55
4.3.1	Influence of feed flowrate on membrane performance	55
4.3.2	Parameter estimation and model fit	57
4.3.3	Influence of feed composition	61
4.3.3.1	Effect of solvent concentration in binary organic-water systems	61
4.3.3.2	Influence of second organic component on butanol recovery in ternary systems	65
4.3.4	Influence of feed stream temperature	70
4.3.4.1	Effect of temperature in binary organic-water systems	70
4.3.4.2	Effect of temperature for butanol recovery in ternary systems	76
4.3.5	Measuring intrinsic coupling in ternary mixtures: Permeance based coupling factors	78
4.4	Summary	82
5	Role of Sorption and Thermodynamic Coupling on Butanol Permeation in Quaternary Mixtures: Thermodynamic and Statistical Modeling	84

5.1	Introduction	84
5.2	Model Development	87
5.3	Results and Discussions	94
5.3.1	Estimation of sorption characteristics	94
5.3.1.1	Equilibrium sorption of pure components in membrane	94
5.4	Parameter estimation, model fit and validation	96
5.4.1	Influence of thermodynamic coupling effects on butanol sorption in quaternary mixtures	101
5.4.1.1	Effect of feed composition and temperature on activity coefficients	101
5.4.1.2	Effect of feed composition and temperature on volume fractions	105
5.4.1.3	Sorption isotherms between activity in feed and volume fractions: Influence of membrane-solvent interaction effects on butanol sorption	116
5.4.2	Influence of thermodynamic coupling effects on butanol permeation in quaternary mixtures	118
5.4.2.1	Effect of feed composition and temperature on butanol fluxes	118
5.4.2.2	Flux isotherms between volume fractions and butanol fluxes: A discussion on origin of flux coupling phenomena	123
5.5	Summary	126
6	Role of Multicomponent Diffusion and Kinetic Coupling on Butanol Permeation : Maxwell Stefan based Formulations	128
6.1	Introduction	128
6.2	Model Development	131
6.3	Results and Discussion	135
6.3.1	Thermodynamic correction factor matrix $[\Gamma]$ and contribution of thermodynamic coupling effect	135
6.3.2	Kinetic coupling effect in ABE solutions and the contribution of plasticization, clustering, and correlation effects towards the correlation matrix	140
6.3.2.1	Estimation of single component MS diffusivities $\mathcal{D}_{im}^V$ from unary permeation	141
6.3.2.2	Estimation, analysis and contribution of self and cross MS diffusivities towards the permeation of binary butanol-water mixtures through the membrane polymer	143
6.3.2.3	Estimation, analysis and contribution of self and cross MS diffusivities towards the permeation of ternary butanol-water-acetone mixtures through the membrane polymer	152
6.3.2.4	Estimation, analysis and contribution of self and cross MS diffusivities towards the permeation of ternary butanol-water-ethanol mixtures through the membrane polymer	158

6.3.2.5	Some observations regarding the origin of kinetic coupling phenomena in permeation of ABE solutions through the studied PDMS membrane	162
6.4	Summary	164
7	Conclusions and Recommendations	167
7.1	Conclusions	167
7.2	Scope for future work	170
	Bibliography	173
	Appendix A Physical and Chemical Properties of Different Feed Components	193
	Appendix B Statistical Indicators for Comparative Analysis of Goodness of Fit and Prediction of Model	198
	Appendix C Modified Sherwood Correlation for the Test Cell Used in the Present Study	202
	Appendix D Additional empirical correlations for calculation of volume fractions and fluxes in quaternary ABE solution (Chapter 5)	206
	Appendix E Generalized analytical derivation of Γ_{ij} matrix elements for multicomponent mixtures	209
	Appendix F Adjustable Parameters and Analysis of Fit for Various Semi-empirical Expressions for Self Diffusivities (Chapter 6)	213
	Publications from Thesis	230
	Bio-Data of Author	231

List of Figures

1.1	Schematic representation of ABE fermentation process for bio-butanol production.	3
1.2	Schematic representing organophilic pervaporation process for biorefining applications and a typical graphical representation of the impact of imposed membrane selectivity in pervaporation on the VLE selectivity [19], α represents the membrane selectivity.	6
1.3	A typical concentration profile and mass transport of component ' i ' through the membrane, where membrane is selective towards the i^{th} component. BL represents the boundary layer.	7
1.4	Schematic depicting the various interaction effects and the resulting coupling effects relevant for butanol recovery from ABE solutions via organophilic pervaporation	10
2.1	Schematic depicting the various interaction effects and the resulting coupling effects relevant for butanol recovery from ABE solutions via organophilic pervaporation	23
2.2	Schematic depicting the various interaction effects and the resulting coupling effects relevant for butanol recovery from ABE solutions via organophilic pervaporation	32
3.1	Schematic diagram of experimental setup for pervaporation	37
4.1	Schematic showing the procedure for model solution	55
4.2	Variation of fluxes and separation factors with feed flowrates for 3 wt. % binary butanol-water mixtures at 313.15 K	56
4.3	Variation of fluxes and separation factors with different feed concentration of solvent in water and model predictions for a) Acetone-Water, b) Ethanol-Water and c) Butanol-Water binary mixtures at 313.15K	62
4.4	Variation of fluxes with changes in butanol concentration in feed and model predictions for ternary solutions with compositions: a) Butanol - 3 wt. % Ethanol - Water mixture and b) Butanol - 3 wt. % Acetone - Water at 313.15K. Relative errors between experimental results and model predictions are also depicted with bar charts.	66

4.5	Variation of fluxes with changes in second component concentration in feed and model predictions for ternary solutions with compositions: a) BEW mixture and b) BAW mixtures with 3wt.% butanol at 313.15K. Relative errors between experimental results and model predictions are also depicted with bar charts	67
4.6	Comparison of changes in butanol fluxes, butanol separation factors, butanol selectivities and butanol permeances with a) feed concentration of butanol and b) feed concentration of second component , between 3 wt.% binary butanol-water mixtures and ternary 3 wt.% butanol – 3 wt.% acetone-water and 3 wt.% butanol - 3 wt.% ethanol - water mixtures	69
4.7	Component fluxes, separation factors and selectivities in ternary butanol-ethanol-water mixtures with variation in a) Butanol concentration in feed b) Ethanol concentration in feed	71
4.8	Component fluxes, separation factors and selectivities in ternary butanol-acetone-water mixtures with variation in a) Butanol concentration in feed b) Acetone concentration in feed	72
4.9	Variation of fluxes and separation factors with temperature and model predictions in 3 wt.% a) Acetone-Water, b) Ethanol-Water and c) Butanol-Water binary mixtures	73
4.10	Variation of fluxes with temperature and model predictions for ternary solutions with compositions: a) BEW mixture and b) BAW mixture with 3wt.% butanol and 1.5 wt.% second component	76
4.11	Comparison of changes in a) butanol fluxes b) butanol separation factors c) butanol selectivities and d) butanol permeances, with temperature between BW mixtures and ternary BEW and BAW mixtures with 3 wt.% butanol and 1.5 wt.% second component	79
4.12	Variation of coupling factors between butanol permeances in ternary BEW and BAW mixtures and corresponding binary BW mixtures with : a) Butanol concentration in feed mixture at 313.15 K ; second component is kept constant at 3 wt.%; c) Concentration of second component in feed mixtures at 313.15K; Butanol concentration is kept constant at 3 wt.%, c) Molar ratios between butanol and second component in different compositions at 313.15 K, and d) Feed temperatures ; mixtures have concentration of 3 wt.% butanol and 1.5 wt.% second component	80
5.1	Schematic depicting the organization of the chapter	87
5.2	Schematic showing the procedure for estimation of adjustable parameters and calculation of volume fractions	93
5.3	Equilibrium volume fractions of pure components at different temperatures	95

5.4	Simulated activity coefficient of butanol (γ_b) exhibiting a : comparison of γ_b in binary BW mixtures and quaternary ABE aqueous solution having 3 wt.% ethanol and 3 wt.% acetone for various models at 313.15 K b : variation with change in composition for UNIQUAC-HB model at 313.15 K c : variation with change in composition for UNIQUAC model at 313.15 K d : variation with change in temperature for UNIQUAC and UNIQUAC-HB model for binary BW mixtures at various concentrations and e : variation with change in temperature for UNIQUAC and UNIQUAC-HB model for and quaternary mixtures having various concentrations of butanol and ethanol, acetone in 3 wt.% each.	102
5.5	Activity coefficient for individual components w.r.t a : butanol wt.% in quaternary ABE-Water mixtures having 3 wt.% acetone and 3 wt.% ethanol and b : Temperature in a 3:3:3 wt.% ABE aqueous mixture	104
5.6	Logworth values and absolute values of parameter estimate for each term in model equations (5.23) and (5.24) for butanol and other solvents	110
5.7	Interaction profiles for ϕ_b as predicted by the UNIQUAC (solid lines) and the UNIQUAC-HB (dotted lines) model depicting the interaction effects between the independent variables: (a, d) : w_b and T , (b, g) : w_e and T , (c, j) : w_a and T , (e, h) : w_b and w_e , (f, k) : w_b and w_a and (i, l) : w_e and w_a . The remaining variable in each panel is kept constant at its respective 0 th level	113
5.8	Response surfaces and contour profiles for ϕ_b in quaternary mixtures as a function of feed composition and depicting variation with a : w_b and w_e , b : w_b and w_e and c : w_a and w_e . Other process variables in each plot are kept constant at their respective 0 th level.	114
5.9	Response surfaces and contour profiles for ϕ_b in quaternary mixtures as a function of feed temperature and depicting variation with a : w_b and T , b : T and w_e and c : w_a and T . Other process variables in each plot are kept constant at their respective 0 th level	116
5.10	Sorption isotherms of butanol (and an enlarged section in b) in PDMS membrane at different feed compositions at 313.15 K as calculated by the UNIQUAC-HB model.	117
5.11	Response surfaces and contour profiles for J_b in quaternary mixtures as a function of feed composition and depicting variation with a : w_b and w_e , b : w_b and w_e and c : w_a and w_e . The concentration of the other solvent in each plot are kept constant at 3 wt.% and temperature at 313.15 K.	120
5.12	Response surfaces and contour profiles for J_b in quaternary mixtures as a function of feed temperature and depicting variation with a : w_b and T , b : T and w_e and c : w_a and T . Other process variables in each plot are kept constant at their respective 0 th level.	121
5.13	Butanol fluxes (mol/m ² hr) versus volume fractions of butanol in the membrane a : as calculated by UNIQUAC model at various compositions and at 313.15 K, b : as calculated by UNIQUAC-HB model at various compositions and at 313.15 K	124

5.14	Butanol fluxes (mol/m ² hr) versus volume fractions of butanol in the membrane at various compositions with total added E+A=6 wt.% at 313.15 K a: as calculated by UNIQUAC model, b: as calculated by UNIQUAC-HB model	125
6.1	Thermodynamic correction factor elements as a function of feed composition for various binary solutions in PDMS membrane at 313.15 K, calculated by the UNIQUAC model	137
6.2	The ratio of effective driving forces $((\Gamma_{bb}\Delta\phi_b + \Gamma_{bw}\Delta\phi_w)/(\Gamma_{bw}\Delta\phi_b + \Gamma_{ww}\Delta\phi_w))$ and ideal driving forces $(\Delta\phi_b/\Delta\phi_w)$ for binary solvent (1)-water (2) systems in Pervap-4060 membranes at 313.15K	138
6.3	Thermodynamic correction factor elements and ratio of effective driving forces and ideal driving forces $(\Delta\phi_b/\Delta\phi_w)$ for ternary butanol (1)-water (2)-ethanol/acetone (3) systems in PERVAP-4060 membranes at 313.15 K .	139
6.4	General algorithm used for modeling of volumetric fluxes in multicomponent mixtures. Details of the Genetic Algorithm and Downhill Simplex are provided in Chapter 3	142
6.5	Experimental Ficks diffusivities D_{im} and MS diffusivities $\mathcal{D}_{im}$ estimated from equations (6.15) and (6.12), respectively and fitted for equation (6.16) for the unary pervaporation of a: ethanol, b: water, c: butanol and d: acetone, through PERVAP-4060 membrane at various operating temperatures.	145
6.6	Analysis of model fit between experimental partial fluxes for binary BW permeation taken from Table 3.3 and those predicted through MS formulations using diffusivities expressions in cases I-IV at various values of cross-diffusivities.	149
6.7	Analysis of model fit between experimental partial fluxes for ternary BAW permeation and those predicted through MS formulations using Clustering Scenario 1 while varying cross-diffusivities as per approach A-C.	154
6.8	Analysis of model fit between experimental partial fluxes for ternary BAW permeation taken from Table 3.4 and those predicted through MS formulations using Clustering Scenario 2 while varying cross-diffusivities as per approach A-C	158
6.9	Analysis of model fit between experimental partial fluxes for ternary BEW permeation taken from Table 3.4 and those predicted through MS formulations using Clustering Scenario 1 while varying cross-diffusivities as per approach A-C.	159
6.10	Analysis of model fit between experimental partial fluxes for ternary BEW permeation taken from Table 3.4 and those predicted through MS formulations using Clustering Scenario 2 while varying cross-diffusivities as per approach A-C. Also represented by the star point is the Combined Clustering Scenario 3 at the assumption of negligible degree of correlation	160
6.11	Comparative model prediction of various clustering scenarios (CS) of solvent fluxes with variation in weight fractions of butanol in feed in binary BW and ternary BEW and BAW systems. The third component and feed temperature are kept constant at 3 wt.% and 313.15 K.	163

7.1	The present state of technology readiness for industrial application for pervaporation for biorefining of ABE biofuels and crucial future research areas needed to advance the technology toward industrial application.	172
A.1	Cross-Sectional images were obtained using Thermofisher Scientific Apreo S Scanning Electron Microscope. Prior to imaging, the samples were sputter-coated with gold using a Quorum Q-150T ES sputter coater. To obtain cross-sectional images, a small portion of the membrane was soaked in hexane for 10 minutes, followed by immersion in liquid nitrogen. Once frozen, the membrane was fractured, and the broken edge was positioned upward on the SEM sample holder.	197
C.1	The concentration profile across the feed side liquid boundary layer for the test cell used in the present study	203

List of Tables

2.1	Mass Transfer Models used to describe mass transfer through membrane in pervaporation in this manuscript	19
3.1	Experimental values of degree of swelling (equation (3.1)), volume fractions (equation (3.2)) of pure solvents in PERVAP-4060 membrane and the calculated pure component densities at different temperatures.	35
3.2	Experimental values of pure component molar fluxes for unary pervaporation at different operating temperatures	40
3.3	Experimental results binary solvent(i)/water systems at different operating temperatures and feed weight fractions	41
3.4	Experimental results ternary butanol(i)/ second component(j)/water systems at different operating temperatures and feed weight fractions	42
3.5	Independent experimental variable for RSM and their respective levels . . .	43
3.6	CCD experimental matrix and observed responses for pervaporation	44
3.7	Parameters used during optimization in <i>ga</i> solver	46
3.8	Parameters used during optimization in <i>fminsearch</i> solver	46
4.1	Values of overall permeance coefficient of butanol (K_i) and liquid boundary layer permeance coefficient ($K_{i,l}$), and polarization index (I) at different feed side Reynolds numbers. w_b is kept constant at 0.03 and and feed temperature is maintained at 313.15 K	57
4.2	Estimated parameters for binary solvent-water systems and goodness of fit and prediction coefficients for component fluxes	58
4.3	Estimated parameters and goodness of fit coefficients for component fluxes in ternary mixtures by ternary model 1	59
4.4	Estimated parameters and goodness of fit and prediction coefficients for component fluxes in ternary mixtures by ternary model 2.	60
4.5	Hansen solubility parameters [130] and interaction radii of various solvents with PDMS membrane.	63
4.6	Values of apparent activation energies of pervaporation (E_{pv}) estimated from equation (26), for binary solvent-water mixtures with 3 wt.% organic content.	74
4.7	Values of apparent activation energies of pervaporation ($E_{i,pv}$) estimated from equation (4.27) for ternary mixtures with 3 wt.% Butanol + 1.5 wt% second component in feed.	77
5.1	Pure component parameter values for solvents and PDMS at 298 K [88,135]	89

5.2	Estimated adjustable parameters a_{ij} and b_{ij} for UNIQUAC model.	97
5.3	Estimated adjustable parameters a_{ij} and b_{ij} for UNIQUAC-HB model. . . .	97
5.4	Estimated adjustable parameters a_{ij} , b_{ij} , and κ_{ij} for M-NRTL model. . . .	98
5.5	MAPE between predicted activity coefficient from various thermodynamic models and experimental VLE data.	99
5.6	Simulated volume percent for CCD matrix with A: UNIQUAC model and B: UNIQUAC-HB model	105
5.7	Summary of fit of regression models for volume fractions	109
5.8	Summary of fit of regression models for flux responses	119
6.1	Values of equilibrium volume fractions (Chapter 5), and Γ_{ii} calculated by the UNIQUAC model (Equations 6.4 and 6.5) for butanol, ethanol, acetone, and water in PDMS at various temperatures.	144
6.2	Pre-exponential Arrhenius parameters and energy of activations for MS diffusivities between 303.15 and 313.15 K.	144
A.1	Molecular formula, molecular weight M, kinematic diameter, critical properties and acentric factor and other physical properties at 313.15 K	194
A.2	Values of coefficients for calculating vapor pressure of pure components at different temperatures	195
A.3	Values of coefficients for calculating densities of pure components at different temperatures	196
A.4	Values of coefficients for calculating viscosities of pure components at different temperatures	196
F.1	Adjustable parameters and analysis of fit for prediction of binary water fluxes by Case I using various mixing rules/degree of correlations	214
F.2	Adjustable parameters and analysis of fit for prediction of binary Butanol-Water fluxes by Case II using various mixing rules/degree of correlations. .	214
F.3	Adjustable parameters and analysis of fit for prediction of binary Butanol-Water fluxes by Case III using various mixing rules/degree of correlations. .	215
F.4	Adjustable parameters and analysis of fit for prediction of binary Butanol-Water fluxes by Case IV using various mixing rules/degree of correlations. .	216
F.5	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-AcO mixtures using Scenario 1 to explain clustering and varying all degrees of correlation equivalently as per Case A.	217
F.6	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-AcO mixtures using Scenario 1 to explain clustering and varying degrees of correlation $\frac{D_{bm}^V}{D_{bw}^V} = \frac{D_{wm}^V}{D_{wj}^V}$ equivalently as per Case B. . .	218
F.7	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Acetone mixtures using Scenario 1 to explain clustering and varying only the degrees of correlation $\frac{D_{bm}^V}{D_{bw}^V}$ as per Case C.	219

F.8	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Acetone mixtures using Scenario 2 to explain clustering and varying all degrees of correlation equivalently as per Case A.	220
F.9	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Acetone mixtures using Scenario 2 to explain clustering and varying degrees of correlation $\mathcal{D}_{bm}^V/\mathcal{D}_{bw}^V = \mathcal{D}_{wm}^V/\mathcal{D}_{wj}^V$ equivalently as per Case B.	221
F.10	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Acetone mixtures using Scenario 2 to explain clustering and varying only the degrees of correlation $\mathcal{D}_{bm}^V/\mathcal{D}_{bw}^V$ as per Case C.	222
F.11	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Ethanol mixtures using Scenario 1 to explain clustering and varying all degrees of correlation equivalently as per Case A.	223
F.12	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Ethanol mixtures using Scenario 1 to explain clustering and varying degrees of correlation $\mathcal{D}_{bm}^V/\mathcal{D}_{bw}^V = \mathcal{D}_{wm}^V/\mathcal{D}_{wj}^V$ equivalently as per Case B.	224
F.13	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Ethanol mixtures using Scenario 1 to explain clustering and varying only the degrees of correlation $\mathcal{D}_{bm}^V/\mathcal{D}_{bw}^V$ as per Case C.	225
F.14	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Ethanol mixtures using Scenario 2 to explain clustering and varying all degrees of correlation equivalently as per Case A.	226
F.15	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Ethanol mixtures using Scenario 2 to explain clustering and varying degrees of correlation $\mathcal{D}_{bm}^V/\mathcal{D}_{bw}^V = \mathcal{D}_{wm}^V/\mathcal{D}_{wj}^V$ equivalently as per Case B.	227
F.16	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Ethanol mixtures using Scenario 2 to explain clustering and varying only the degrees of correlation $\mathcal{D}_{bm}^V/\mathcal{D}_{bw}^V$ as per Case C.	228
F.17	Adjustable parameters and analysis of fit for prediction of fluxes in ternary Butanol-Water-Ethanol mixtures using Combined Clustering Scenario 3 with the assumption of negligible degrees of correlation.	229

Abbreviations

A or AcO	A cetone
B or BuOH	B utanol
E or EtOH	E thanol
W	W ater
VLE	V apor- L iquid E quilibrium
PDMS	P oly(d imethylsiloxane)
OVAT	O ne V ariable at a T ime
DOE	D esign of E xperiment
RSM	R esponse S urface M ethodology
HSP	H ansen S olubility P arameter
MS	M axwell- S tefan
FID	F lame I onization D etector
C-CCD	C ircumscribed C entral C omposite D esign
GA	G enetic A lgorithm
RMSE	R oot M ean S quared E rror
rRMSE	r elative R oot M ean S quared E rror
MAPE	M ean A bsolute P ercentage E rror
ANOVA	A nalysis of N ariance
adj	A djoint of matrix
det	D eterminant of matrix

Symbols

A_{ij}	Adjustable parameter between the i^{th} and j^{th} component
a_{ij}	Adjustable parameter between the i^{th} and j^{th} component
a_{CP}	Boundary layer parameter (m^{-1})
a	Activity
A_r	Area of membrane (m^2)
α	Intrinsic selectivity
η	Viscosity (Pa s)
β	Separation factor
b_{ij}	Adjustable parameter between the i^{th} and j^{th} component
b_{CP}	Boundary layer parameter
$C_i(x_i)$	Coupling factor for component i at concentration x_i
χ	Empirical coefficient in regression equation
δ	Thickness of membrane active layer (m)
Δ_d	Dispersion solubility parameter ($MPa^{1/2}$)
Δ_h	Hydrogen-bonding solubility parameter ($MPa^{1/2}$)
Δ_p	Polar solubility parameter ($MPa^{1/2}$)
D	Diffusivity (m^2/s)
d	Semi cell thickness at the edge of test cell (m)
$D.f$	Driving force
E_D	Activation energy of diffusivity ($kJ\ mol^{-1}$)
E_γ	Coefficient in Clausius Clapeyron equation ($kJ\ mol^{-1}$)
E_{evap}	Energy of evaporation ($kJ\ mol^{-1}$)
E_p	Activation energy of permeation of component i ($kJ\ mol^{-1}$)

E_{pv}	Activation energy of pervaporation (kJ mol ⁻¹)
E_S	Activation energy of solubility (kJ mol ⁻¹)
ϵ	Semiempirical plasticization coefficient
ε	Tolerance for error
f^{sat}	Fugacity at saturation pressure
f^v	Fugacity of vapor phase
f_i	Fugacity coefficient
G_{ij}	Interaction parameter between the <i>i</i> th and the <i>j</i> th component
Γ	Thermodynamic correction factor matrix
I	Polarization Index
J	Molar diffusive flux (mol m ⁻² s ⁻¹)
j	Mass flux (kg m ⁻² s ⁻¹)
k_l	Mass transfer coefficient in the liquid side boundary layer (m/s)
K	Overall permeance coefficient (mol m ⁻² Pa ⁻¹ s ⁻¹)
K_l	Liquid boundary layer permeance coefficient (mol m ⁻² Pa ⁻¹ s ⁻¹)
K_m	Membrane permeance coefficient (mol m ⁻² Pa ⁻¹ s ⁻¹)
κ_{ij}	Non-randomness parameter between the <i>i</i> th and <i>j</i> th component
μ	Chemical potential
M	Molecular weight (mol kg ⁻¹)
$\bar{V}$	Partial molar volume (m ³ /mol)
N_c	Number of components in the liquid feed mixture
N_e	Total number of experimental data points
N^V	Volumetric flux (m ³ / m ² s)
P	Pressure in permeate channel (Pa)
P^{sat}	Vapor pressure of component (Pa)
q	Area/Surface parameter of pure component
r	Volume parameter of pure component
R	Gas constant (J mol ⁻¹ K ⁻¹)
R^2	Coefficient of Determination
R_{adj}^2	Adjusted coefficient of Determination
Re_R	Reynolds number at the cell edge

ρ	Mass density (kg/m ³)
ρ^{mol}	Molar density (mol/m ³)
S	Degree of swelling
S	Solubility coefficient (mol m ⁻³ Pa ⁻¹)
Sc	Schmidt Number
t	Time (s)
τ_{ij}	Interaction parameter between the $\mathbf{i}^{th}$ and the $\mathbf{j}^{th}$ component
θ	Area fraction
u	Velocity of/in feed stream (m s ⁻¹)
U	Uncoded Variable
V^L	Liquid phase molar volume (m ³ /mol)
w	Weight fraction
W	Weight (kg)
X	Coded Variable in RSM
x	Mole fraction in liquid feed
y	Mole fraction in permeate
Y	Response Variable in RSM
Z	Coordination number
z	Axial coordinate along thickness of the membrane (m)
ω	Distance of star points from the central point in RSM
ξ	Clustering constant
$[B]$	Diffusional matrix in MS formulations (s/m ²)
$[B]^{-1}$	Inverse diffusional matrix (m ² /s)
D_{ij}	MS cross-diffusivity (m ² /s)
D_{ij}^V	Modified MS cross-diffusivity (m ² /s)
D_{im}^V	MS self-diffusivity (m ² /s)

Subscripts

i, j, k	Component i, j, k in the mixture
m	Membrane
dry	In dry membrane
wet	In wetted swollen membrane
tot	Total components
b	Butanol
e	Ethanol
a	Acetone
w	Water
exp	Experimental reading
theo	Model prediction
bulk	Bulk liquid in feed stream
l	Liquid component
s	Organic solvent
p	Permeate
0	At the upstream (feed side) interface of the membrane
δ	At the downstream (vacuum side) interface of the membrane

Superscripts

o	For pre-exponential factors
f	In liquid feed phase
m	In membrane phase
cen	Denotes central point of the design matrix
C	Depicts combinatorial term
R	Depicts Residual term
'	Depicts Modified parameters for UNIQUAC-HB
exp	Experimental reading
cal	Model calculation
-	Averaged quantity
~	For pre-exponential factors
`	Considering water as a plasticizing component
tern	In ternary mixtures
bin	In binary mixtures
-1	Inverse of the matrix
con	Conjoint of the matrix
T	Transpose of the matrix

Outline of Thesis

A concise overview of the organization of the dissertation is outlined as follows:

Chapter 1: Introduces the research problem of this thesis, focusing on the advantages and challenges associated with adapting pervaporation for biorefining of multicomponent fermentation systems. It emphasizes the potential of organophilic pervaporation for biobutanol recovery while providing a general theoretical background to familiarize the reader with the basic concepts related to pervaporation and multicomponent coupling phenomena.

Chapter 2: An exhaustive literature review is presented regarding the nature of coupling phenomena and multicomponent permeation in pervaporation of ABE solutions. The choice for membrane selection is justified. A detailed review of the established modeling techniques for multicomponent pervaporation is also included underlining the scope and drawbacks of each. The rationale and motivation for defining objectives of research is developed based on the gaps highlighted in literature.

Chapter 3: Provides an elaborate description of the experimental methodology and model solution techniques used in the present study. The experimental design, analytical techniques, and membrane performance evaluation metrics are presented, along with the methods for parameter estimation, model solution, and validation.

Chapters 4 to 6 sequentially present the results and discussion part of this study.

Chapter 4 : Membrane permeation in binary and ternary ABE solutions is studied to describe and isolate the effect of added acetone and ethanol on transport of butanol

through the membrane . Modified solution diffusion models are developed to gain insights into the nature and magnitude of coupling effect at different operating conditions.

Chapter 5 : Sorption characteristics and influence of thermodynamic coupling effects on butanol permeation in quaternary ABE solutions are studied. Various local composition thermodynamic models and statistically validated regression models are developed to uncover significance of interaction effects and sorption on final butanol fluxes in quaternary mixtures.

Chapter 6 : The nature and origin of coupling phenomena is investigated . The resolution of thermodynamic and kinetic coupling effects is aided by the exhaustive analysis of Maxwell-Stefan formulations and MS diffusivities derived for multicomponent systems. The role of diffusive or kinetic coupling on permeation of butanol is addressed.

Chapter 7: Overall conclusions from this work are summarized , highlighting its limitations. Recommendations are provided for future research.