STATUS OF THESIS

Title of thesis	Studies on CO_2 solubility in *N*-Methyldiethanolamine and hydrophobic ionic liquid binary mixtures

I MAJID MAJEED AKBAR
do hereby allow my thesis to be placed at the Information Resource Center (IRC) of Universiti Teknologi PETRONAS (UTP) with the following conditions:

1. The thesis becomes the property of UTP
2. The IRC of UTP may make copies of the thesis for academic purposes only.
3. This thesis is classified as

☐ Confidential

☑ Non-confidential

If this thesis is confidential, please state the reason:
_____
_____
_____

The contents of the thesis will remain confidential for _____ years.

Remarks on disclosure:
_____
_____
_____

Endorsed by

_____ _____
Signature of Author Signature of Supervisor

Permanent address:
245-D-II, Wapda Town, Lahore,
Pakistan.

Name of Supervisor
Prof. Dr. Thanabalan Murugesan

Date : _____ Date : _____

UNIVERSITI TEKNOLOGI PETRONAS

THERMOPHYSICAL PROPERTIES AND CO_2 SOLUBILITY IN IONIC LIQUIDS, *N*-METHYLDIETHANOLAMINE AND THEIR BINARY MIXTURES

by

MAJID MAJEED AKBAR

The undersigned certify that they have read, and recommend to the Postgraduate Studies Programme for acceptance of this thesis for the fulfillment of the requirements for the degree stated.

Signature: _____

Main Supervisor: Prof. Dr. Thanabalan Murugesan

Signature: _____

Head of Department: Dr. Suriati Sufian

Date: _____

STUDIES ON CO_2 SOLUBILITY IN *N*-METHYLDIETHANOLAMINE AND HYDROPHOBIC IONIC LIQUID BINARY MIXTURES

by

MAJID MAJEED AKBAR

A Thesis

SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAMME

AS A REQUIREMENT FOR THE DEGREE OF

DOCTOR OF PHILOSOPY IN CHEMICAL ENGINEERING

CHEMICAL ENGINEERING DEPARTMENT

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR,

PERAK

MAY 2013

DECLARATION OF THESIS

Title of thesis | STUDIES ON CO_2 SOLUBILITY IN *N*-METHYLDIETHANOLAMINE AND HYDROPHOBIC IONIC LIQUID BINARY MIXTURES

I MAJID MAJEED AKBAR

do hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

Witnessed by

_____ _____

Signature of Author | Signature of Supervisor

Permanent address:
245-D-II, Wapda Town, Lahore, Pakistan.

Name of Supervisor
Prof. Dr. Thanabalan Murugesan

Date : _____ Date : _____

To my Parents,

To my Brothers; Engr. Khalid, Dr. Tariq, Engr. Abid,

To my wife Memmona,

To my Son Sanan Majid

ACKNOWLEDGEMENTS

All the praises for Almighty Allah, whose uniqueness, oneness and wholeness are unchangeable, guided us in lacerate and congenial circumstances. All respects for the Holy Propher Hazrat Muhammad (PBUH), who enabled us to recognize our creator.

I am highly indebted to my supervisor Prof. Dr. Thanabalan Murugesan. He deserves a great deal of credit, due to his kind encouragement, able guidance and intellectual discerning power; I have been able to complete this work. He always provided generous time for technical discussions and guided me in each and every step of this research. I am extremely thankful to Dr. Khashayar, for his kind support and value able time rendered for technical discussions. I am grateful to the administration of the Universiti Teknologi PETRONAS (UTP) and its Chemical Engineering Department. Staff members of UTP library and laboratories deserve a great deal of credit for providing conducive environment to the researchers during their studies. I am thankful to the numerous unknown reviewers who helped to improve this work. I express my heartedly and deep feelings to all my family members, especially my father, Dr. Akbar Ali, who has always taught me to be a good human being and urged for higher education. My mother, at the knees of her, I learnt every aspect of life, she has always encouraged me to be courteous and helpful to others. My brothers, Engr. Khalid Saeed Akbar, Dr. Tariq Saeed Akbar, Engr. Abid Majeed Akbar and my loving sisters (Shabnum, Robina, Samina) and their families (Imtiaz, Rafique, Rehmat) deserve a great deal of credit. I am thankful to my sister in law Sheza Khilji for providing necessary research papers. I am very much grateful to all my friends, Junaid, Subhan, Ayoub, Naseeb, Sikandar, Murshid, Anees and Awais, for their support and motivation to achieve this goal. Finally, I would like to thank my beloved wife (Memmona) for providing such a wonderful companionship and help to accomplish this task. She always gave me every kind of support and encouragement and without her help this work would have not been completed. I pray for the departed loved one (My Mamoo, Khala, Phopo) who passed away during my stay in Malaysia.

ABSTRACT

A fundamental and systematic investigation on the potential application of hybrid mixtures {comprising of ionic liquid (IL) + MDEA} for CO_2 removal has been presented. The binary mixtures of three imidazolium based ILs namely; 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([hmim][FAP]) with *N*-methyldiethanolamine (MDEA) were prepared and the CO_2 solubility was measured in the pure solvents as well as in the binary mixtures at three temperatures (298.15, 313.15, 323.15) K and at eight different pressures (≤ 3000 kPa). Prior to CO_2 solubility the basic thermophysical properties (ρ, η, n_D, TGA) were established. The excess properties namely; excess molar volumes, viscosity and refractive index deviation were deduced from the measured physical properties. The effects of pressures, temperatures, concentrations, and anions on CO_2 solubility were studied in detail. The temperature depended parameters of solubility namely; Henry's constants, enthalpy, entropy were also deduced. The experimental CO_2 solubility results were modelled with the help of Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) equations of states (EOS) with van der Waals (vdW) and Mathias-Klotz-Prausnitz (MK) mixing rules. The pure liquids and the selected binary mixtures which were once used for CO_2 solubility were regenerated and used again to investigate their potential applicability for recycling. The PR EOS with MK mixing rule yielded good results in comparison to the PR-vdW, SRK-MK and SRK-vdW. The solvent regeneration studies validated the potential of these solvents for recycling purposes, as fresh and recycled solvents showed almost identical solubility values. The binary mixtures of ILs ([hmim][FAP], [hmim][Tf_2N]) with MDEA exhibited lower values of CO_2 solubility in comparison to pure ILs at all concentrations. The binary mixtures of IL ([hmim][BF_4]) with MDEA at concentrations {1:4, 1:1 (molar ratio of IL to MDEA)} showed slightly higher values of absorption in comparison to the pure IL. The display of lower values of CO_2 solubility in the binary mixtures ([hmim][FAP]+MDEA, [hmim][Tf_2N]+MDEA) and inappreciable enhancement in ([hmim][BF_4] + MDEA) binary mixtures led to

investigate more binary {MDEA + ILs (other than [hmim][BF_4], [hmim][FAP], [hmim][Tf_2N])} and even ternary (IL + amine + water) mixtures for CO_2 solubility. It was done to investigate that whether these mixtures display the same trend (decreased or substantially increased solubility) or show appreciably high CO_2 solubility. The binary mixtures of ILs namely: bis(2-hydroxyethyl)ammonium acetate ([bheaa]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([bmim][FAP]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) with MDEA were used for CO_2 solubility. The aqueous IL solutions used for CO_2 solubility were comprised of the ILs: 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([emim][FAP]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]) with monoethanolamine (MEA) or diethanolamine (DEA). The same trends were observed for the case of binary mixtures that CO_2 solubility decreased and in some cases increased substantially. The binary mixtures of ILs ([bmim][FAP], [bmim][Tf_2N]) with MDEA showed lower values of solubility than pure ILs. The binary mixtures of ILs ([bmim][BF_4], [bheaa]) with MDEA showed slightly higher values of solubility. The aqueous mixtures of ILs showed lower values of solubility than aqueous amine solutions. The addition of IL (at all concentrations) did not prove fruitful to aqueous amine solutions in terms of CO_2 solubility.

.

ABSTRAK

Sebuah kajian asas dan sistematik tentang potensi applikasi campuran hibrid (terdiri daripada cecair berion + MDEA) untuk penyingkiran CO_2 telah ditunjukkan. Campuran binary tiga imidazolium berasaskan ILs iaitu; 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4]), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([hmim][FAP]) dengan N-methyldiethanolamine (MDEA) telah disediakan dan kelarutan CO_2 telah diukur di dalam pelarut tulen sebagaimana di dalam campuran binary pada tiga suhu (298.15, 313.15, 323.15) K dan pada lapan tekanan yang berlainan (≤ 3000 kPa). Sebelum kepada kelarutan CO_2 ciri-ciri termofizikal asas (ρ, η, n_D, TGA) dibangunkan. Ciri-ciri lebihan seperti; isipadu molar berlebihan, kelikatan dan sisihan indeks biasan telah disimpulkan daripada ciri-ciri fizikal yang diukur. Kesan tekanan,suhu, kepekatan dan anion pada kelarutan CO_2 telah dikaji secara terperinci. Parameter bergantungan suhu bagi kearutan iaitu; pemalar Henry, entalpi, entropi telah disimpulkan. Keputusan eksperimen kelarutan CO_2 telah dimodelkan dengan bantuan persamaan keadaan Peng-Robinson (PR) dan Soave-Redlich-Kwong (SRK) dengan van der Waals dan Klotz-Prausnitz (MK) undang-undang campuran. Cecair asli dan campuran binary terpilih yang mana digunakan untuk kelarutan CO_2 telah dijanakan dan digunakan kembali untuk mengkaji potensi aplikasi bagi kitar semula. PR EOS dengan undang-undang campuran MK menghasilkan keputusan yang bagus berbanding dengan PR-vdW, SRK-MK dan SRK-vdW. Kajian penjanaan pelarut mengesahkan potensi pelarut bagi tujuan kitar semula, sebagaimana pelarut baru dan kitar semula menunjukkan nilai kelarutan yang hampir sama. Campuran binary ILs ([hmim][FAP], [hmim][Tf_2N]) dengan MDEA menunjukkan nilai kelarutan CO_2 lebih rendah berbanding ILs asli pada kesemua kepekatan. Campuran binari IL ([hmim][BF_4]) dengan MDEA pada kepekatan {1:4, 1:1 (ratio molar IL kepada MDEA)} menunjukkan nilai penyerapan yang sedikit tinggi berbanding IL asli. Paparan nilai kelarutan CO_2 yang rendah dalam campuran binari ([hmim][FAP]+MDEA, [hmim][Tf_2N]+MDEA) dan peningkatan yang tidak ketara

dalam campuran binari ([hmim][BF_4] + MDEA) telah mendorong kepada kajian binari lain {MDEA + ILs (other than [hmim][BF_4], [hmim][FAP], [hmim][Tf_2N])} dan campuran ternari sekata (IL + amine + air) bagi kelarutan CO_2. Ia telah dilakukan bagi mengkaji samada campuran-campuran ini menunjukkan trend yang sama (penurunan atau peningkatan kelarutan yang ketara) atau menunjukkan kelarutan CO_2 yang tinggi yang ketara. Campuran binari bagi ILs iaitu: bis(2-hydroxyethyl)ammonium acetate ([bheaa]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([bmim][FAP]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) with MDEA telah digunakan bagi kelarutan CO_2. Larutan akues IL yang digunakan untuk kelarutan CO_2 terdiri daripada ILs: 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([emim][FAP]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf_2N]) dengan monoethanolamine (MEA) atau diethanolamine (DEA). Trend yang sama turut diperhatikan bagi kes campuran binari yang kelarutan CO_2 menurun dan kes yang lain meningkat dengan ketaranya. Campuran binari ILs ([bmim][FAP], [bmim][Tf_2N] dengan MDEA menunjukkan nilai kelarutan yang rendah berbanding ILs asli. Campuran binari ILs ([bmim][BF_4], [bheaa]) dengan MDEA menunjukkan nilai kelarutan yang sedikit tinggi. Campuran akues ILs menunjukkan nilai yang rendah bagi kelarutan berbanding larutan akues amine. Penambahan IL (pada kesemua kepekatan) tidak membuktikan keberhasilan untuk larutan akues amine dalam terma kelarutan CO_2.

In compliance with the terms of the Copyright Act 1987 and the IP Policy of the university, the copyright of this thesis has been reassigned by the author to the legal entity of the university,

Institute of Technology PETRONAS Sdn Bhd.

Due acknowledgement shall always be made of the use of any material contained in, or derived from, this thesis.

© MAJID MAJEED AKBAR, 2013
Institute of Technology PETRONAS Sdn Bhd
All rights reserved.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

[hmim][BF_4]	1-hexyl-3-methylimidazolium tetrafluoroborate
[hmim][Tf_2N]	1-hexyl-3-methylimidazolium bis(trifluorosulfonyl)imide
[hmim][FAP]	1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
MDEA	*N*-Methyldiethanolamine
PSA	Pressure swing adsorption
TSA	Temperature swing adsorption
ESA	Electric swing adsorption
TEGMME	Triethylene glycol monomethyl ether
DEG	Diethylene glycol
TEG	Triethylene glycol
NFM	*N*-formyl morpholine
DME	Dimethyl ether
DEPEG	Diethyl polyethylene glycol
MEA	Monoethanolamine
AMP	2-amino-2-methyl-1-propanol
PZ	Piperazine
DEA	Diethanolamine
DGA	Diglycolamine
DIPA	Di-isopropanolamine
Am	Amine
IL	Ionic liquid
ILs	Ionic liquids
RTIL	Room temperature ionic liquid

TSIL	Task specific ionic liquid
TGA	Thermogravimetric analysis
aq.MDEA	aqueous *N*-methyldiethanolamine
P	Pressure
x	mole fraction
x_{MDEA}	mole fraction of MDEA
x_{CO2}	mole fraction of carbon dioxide
TEA	Triethanolamine
wt %	Weight percentage
V^E	Excess molar volume
n_D	Refractive index
Δn_D	Refractive index deviation
EOS	Equation of state
PR	Peng Robinson equation of state
SRK	Soave Redlich Kwon equation of state
vdW	van der Waals mixing rule
MK	Mathias Klotz Prautniz mixing rule
T_c	Critical temperature
P_c	Critical pressure
Greek Symbols	
ρ	density
η	Viscosity
$\Delta\eta$	Viscosity deviation
ω	Acentric factor