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THERMOPHYSICAL PROPERTIES AND CO₂ SOLUBILITY IN IONIC
LIQUIDS, *N*-METHYLDIETHANOLAMINE AND THEIR BINARY MIXTURES

by

MAJID MAJEED AKBAR

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STUDIES ON CO₂ SOLUBILITY IN *N*-METHYLDIETHANOLAMINE AND
HYDROPHOBIC IONIC LIQUID BINARY MIXTURES

by

MAJID MAJEED AKBAR

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STUDIES ON CO₂ 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.

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To my Parents,
To my Brothers; Engr. Khalid, Dr. Tariq, Engr. Abid,
To my wife Memmona,
To my Son Sanan Majid

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ABSTRACT

A fundamental and systematic investigation on the potential application of hybrid mixtures {comprising of ionic liquid (IL) + MDEA} for CO₂ removal has been presented. The binary mixtures of three imidazolium based ILs namely; 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF₄]), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([hmim][FAP]) with *N*-methyldiethanolamine (MDEA) were prepared and the CO₂ 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 (\leq 3000 kPa). Prior to CO₂ 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 CO₂ solubility were studied in detail. The temperature depended parameters of solubility namely; Henry's constants, enthalpy, entropy were also deduced. The experimental CO₂ 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 CO₂ 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][Tf₂N]) with MDEA exhibited lower values of CO₂ solubility in comparison to pure ILs at all concentrations. The binary mixtures of IL ([hmim][BF₄]) 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 CO₂ solubility in the binary mixtures ([hmim][FAP]+MDEA, [hmim][Tf₂N]+MDEA) and inappreciable enhancement in ([hmim][BF₄] + MDEA) binary mixtures led to

investigate more binary {MDEA + ILs (other than [hmim][BF₄], [hmim][FAP], [hmim][Tf₂N])} and even ternary (IL + amine + water) mixtures for CO₂ solubility. It was done to investigate that whether these mixtures display the same trend (decreased or substantially increased solubility) or show appreciably high CO₂ solubility. The binary mixtures of ILs namely: bis(2-hydroxyethyl)ammonium acetate ([bheaa]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([bmim][FAP]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]) with MDEA were used for CO₂ solubility. The aqueous IL solutions used for CO₂ solubility were comprised of the ILs: 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([emim][FAP]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]) with monoethanolamine (MEA) or diethanolamine (DEA). The same trends were observed for the case of binary mixtures that CO₂ solubility decreased and in some cases increased substantially. The binary mixtures of ILs ([bmim][FAP], [bmim][Tf₂N]) with MDEA showed lower values of solubility than pure ILs. The binary mixtures of ILs ([bmim][BF₄], [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 CO₂ solubility.

ABSTRAK

Sebuah kajian asas dan sistematik tentang potensi aplikasi campuran hibrid (terdiri daripada cecair berion + MDEA) untuk penyingkiran CO₂ telah ditunjukkan. Campuran binary tiga imidazolium berasaskan ILs iaitu; 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF₄]), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf₂N]), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([hmim][FAP]) dengan N-methyldiethanolamine (MDEA) telah disediakan dan kelarutan CO₂ 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 CO₂ ciri-ciri termofizikal asas (ρ , η , n_D , TGA) dibangunkan. Ciri-ciri lebih 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 CO₂ telah dikaji secara terperinci. Parameter bergantung suhu bagi kelarutan iaitu; pemalar Henry, entalpi, entropi telah disimpulkan. Keputusan eksperimen kelarutan CO₂ 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 CO₂ 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][Tf₂N]) dengan MDEA menunjukkan nilai kelarutan CO₂ lebih rendah berbanding ILs asli pada kesemua kepekatan. Campuran binari IL ([hmim][BF₄]) 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 CO₂ yang rendah dalam campuran binari ([hmim][FAP]+MDEA, [hmim][Tf₂N]+MDEA) dan peningkatan yang tidak ketara

dalam campuran binari ([hmim][BF₄] + MDEA) telah mendorong kepada kajian binari lain {MDEA + ILs (other than [hmim][BF₄], [hmim][FAP], [hmim][Tf₂N])} dan campuran ternari sekata (IL + amine + air) bagi kelarutan CO₂. Ia telah dilakukan bagi mengkaji samada campuran-campuran ini menunjukkan trend yang sama (penurunan atau peningkatan kelarutan yang ketara) atau menunjukkan kelarutan CO₂ yang tinggi yang ketara. Campuran binari bagi ILs iaitu: bis(2-hydroxyethyl)ammonium acetate ([bheaa]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([bmim][FAP]), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]) with MDEA telah digunakan bagi kelarutan CO₂. Larutan akues IL yang digunakan untuk kelarutan CO₂ terdiri daripada ILs: 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([emim][FAP]), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([emim][Tf₂N]) dengan monoethanolamine (MEA) atau diethanolamine (DEA). Trend yang sama turut diperhatikan bagi kes campuran binari yang kelarutan CO₂ menurun dan kes yang lain meningkat dengan ketaranya. Campuran binari ILs ([bmim][FAP], [bmim][Tf₂N]) dengan MDEA menunjukkan nilai kelarutan yang rendah berbanding ILs asli. Campuran binari ILs ([bmim][BF₄], [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 CO₂.

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LIST OF ABBREVIATIONS

[hmim][BF ₄]	1-hexyl-3-methylimidazolium tetrafluoroborate
[hmim][Tf ₂ N]	1-hexyl-3-methylimidazolium bis(trifluorosulfonyl)imide
[hmim][FAP]	1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate
MDEA	<i>N</i> -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	<i>N</i> -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
<i>Am</i>	Amine
IL	Ionic liquid
ILs	Ionic liquids
RTIL	Room temperature ionic liquid

TSIL	Task specific ionic liquid
TGA	Thermogravimetric analysis
aq.MDEA	aqueous <i>N</i> -methyldiethanolamine
P	Pressure
x	mole fraction
x_{MDEA}	mole fraction of MDEA
x_{CO_2}	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