PHYSICAL PROPERTIES OF GUANIDINIUM TRIFLUOROMETHANESULFONATE-METHYLDIETHANOLAMINE AQUEOUS MIXTURES AND THEIR CO_2 ABSORPTION CAPACITIES

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ABSTRACT

In this work, the physical properties *i.e.* density, viscosity and CO_2 solubility studies were conducted on the aqueous systems of *N*-methyldiethanolamine (MDEA) and guanidinium trifluoromethanesulfonate [gua][OTf]. The studies were carried out at various concentration of MDEA (1 – 4 M) and [gua][OTf] (0.1 – 2 M). The temperature and pressure were also varied depending on the study involved.

The studies on densities and viscosities of binary ([gua][OTf] - H_2O) and ternary ([gua][OTf] - MDEA - H_2O) systems were carried out at a wide temperature range from 293 to 363 K and at atmospheric pressure. The results show that the density and viscosity were strongly affected by the presence of water. Correlations for both viscosity and density for binary and ternary systems were ± 3.5 % in temperature ranges from 293 and 363 K except 2M2G and 1M3G have shown deviation up to 9.587 %. Also, binary systems of [gua][OTf] – H_2O *i.e.* 0M0.1G, 0M0.3G, 0M0.5G, 0M0.7G, 0M0.9, 0M1G and 0M4G showed higher deviation in viscosities which is up to 8.442 %.

As for solubility studies, this work was focused in determining the ability of aqueous binary ([gua][OTf] – H_2O) and ternary (MDEA – [gua][OTf] – H_2O) systems in capturing CO_2 at high pressures. The experiments were conducted at CO_2 partial pressures from 500 to 3000 kPa and temperatures at 303, 323 and 333 K. It has been found that the effect of partial pressures was most pronounced for 1 M aqueous [gua][OTf] (0M1G) which showed a competitive performance in capturing CO_2, up to 1.63 mol CO_2/ total mol system at 323.2 K and 3000 kPa, as compared to

other pure ionic liquids such as [emim][C_2N_3], [emim][$MDEGSO_4$] and [emim][OTf] with 0.8132, 0.9587 and 1.0753 mol CO_2/ total mol system, respectively, which were also recorded in the same environments. The solubility to pressure data also supported that 0M1G is involved mainly in physical absorption and the effect of partial pressure was more significant at lower alkanolamine concentration. Correlations of solubility as a function of pressure and temperature have been determined with difference of ± 0.957 %.

The solubility was also measured at lower partial pressure of CO_2 at 10, 50 and 100 kPa and temperature 303.2 K. This experiment was predominantly on chemical absorption and it showed that the addition of 1 M [gua][OTf] induced 14 % of CO_2 solubility at 303.2 K and 100 kPa of the CO_2 partial pressure as compared to 1 M [bmim][BF_4], in 4 M MDEA. Also, the solubility of CO_2 in 4 M [gua][OTf] gave 27.5 % higher CO_2 loading compared to 1 M [gua][OTf]. Compared to 4 M MDEA, the CO_2 loading of blended system 4M1G was found to be slightly lower *i.e.* 0.6498 mol CO_2/ total mol system at 100 kPa. The presence of [gua][OTf] could not make up the loss of the CO_2 absorption capacity of MDEA due to the reducing amount of water with increasing amount of [gua][OTf] as physical absorption of CO_2 will only play a significant role at high operating pressure. The R^2 values from plot of P_{CO2} *versus* ($\alpha_{CO_2}^2$/ 1 - α_{CO_2}) range from 0.94232 to 0.96272 for partial pressure between 0 - 100 kPa. These R^2 values were finely fitted.

ABSTRAK

Kajian mengenai ciri-ciri fizikal seperti ketumpatan, kelikatan and kelarutan CO_2 bagi sistem *N*-methyldiethanolamine (MDEA) (1 – 4 M) dan guanidinium trifluorometanasulfonat [gua][OTf] (0.1 – 2 M) telah dilakukan. Suhu dan tekanan dipelbagaikan bergantung kepada kajian yang terlibat.

Kajian mengenai ketumpatan dan kelikatan sistem binari ([gua][OTf] - H_2O) dan ternari ([gua][OTf] - MDEA - H_2O) dijalankan pada tekanan atmosfera dan suhu bermula 293 ke 363 K. Keputusan eksperimen menunjukkan ketumpatan dan kelikatan dipengaruhi oleh kuantiti air dalam sistem. Peratus perbezaan antara kelikatan dan ketumpatan yang didapati dari eksperimen dan pengiraan bagi sistem binari dan ternari adalah ± 3.5 % pada suhu antara 293 dan 363 K kecuali 2M2G dan 1M3G yang menunjukkan 9.587 %. Dalam pada itu, sistem binari [gua][OTf] – H_2O *i.e.* 0M0.1G, 0M0.3G, 0M0.5G, 0M0.7G, 0M0.9, 0M1G dan 0M4G menunjukkan perbezaan kelikatan yang lebih besar sehingga 8.442 %.

Manakala, bagi kelarutan CO_2, kajian ini memberi fokus kepada penentuan kebolehan sistem akuas binari ([gua][OTf] – H_2O) dan ternari (MDEA – [gua][OTf] – H_2O) dalam menjerap CO_2 pada tekanan tinggi. Eksperimen dijalankan pada tekanan separa CO_2 bermula dari 500 ke 3000 kPa dan suhu pada 303, 323 dan 333 K. Kajian mendapati kesan tekanan separa paling ketara pada 1 M akuas [gua][OTf] (0M1G) yang mana turut menunjukkan kelarutan CO_2 sebanyak 1.63 mol CO_2/ jumlah mol sistem pada 323.2 K dan 3000 kPa, berbanding cecair ionik yang lain seperti [emim][C_2N_3], [emim][$MDEGSO_4$] dan [emim][OTf] dengan 0.8132, 0.9587

and 1.0753 mol CO_2/ jumlah mol sistem yang mana turut dicatat pada keadaan yang sama. Kesan ketara terhadap kelarutan CO_2 oleh 0M1G pada perubahan tekanan separa turut membuktikan sistem tersebut melibatkan penjerapan fizikal secara kesuluruhan dan turut memberi kesan ketara kepada alkanolamina yang berkepekatan lebih rendah. Hubungkait antara kelarutan, tekanan dan suhu telah ditentukan dengan ketepatan $\pm$ 0.957 %.

Kelarutan juga diukur pada tekanan separa CO_2 yang lebih rendah iaitu 10, 50 dan 100 kPa dan suhu 303.2 K. Eksperimen ini melibatkan penjerapan kimia dan keputusan menunjukkan penambahan 1 M [gua][OTf] menaikkan kelarutan CO_2 sebanyak 14 % pada 303.2 K dan 100 kPa berbanding 1 M [bmim][BF$_4$] terhadap 4 M MDEA. Di samping itu, kelarutan CO_2 terhadap 4 M [gua][OTf] meningkat 27.5 % berbanding 1 M [gua][OTf]. Kelarutan 4M1G pula adalah lebih rendah berbanding 4M0G iaitu sebanyak 0.6498 mol CO_2/ jumlah mol sistem pada 100 kPa. Kehadiran [gua][OTf] mengurangkan kelarutan ternari sistem berikutan pengurangan kuantiti air dengan penambahan jumlah [gua][OTf] yang mana penjerapan fizikal hanya berkesan pada operasi bertekanan tinggi. Nilai R^2 dari plot P_{CO2} *versus* ($\alpha_{CO_2}^2$/ 1 - α_{CO_2}) adalah antara 0.94232 ke 0.96272 bagi tekanan separa 0 - 100 kPa. Nilai R^2 telah ditentukan dengan tepat.

ACKNOWLEDGEMENT

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NOMENCLATURE

AGR	Acid gas removal process
PFD	Process flow diagram
GHG	Greenhouse gas
ESRL	Earth systems research laboratory
NOAA	National oceanic and atmospheric administration
CCS	Carbon capture and storage
MDEA	*N*-methyldiethanolamine
MEA	Monoethanolamine
DEA	Diethanolamine
DETA	Diethylenetriamine
PZ	Piperazine
AMP	2-amino-2-methyl-1-propanol
DIPA	Diisopropanolamine
DGA	Diglycolamine
AEEA	Diamine 2-[(2-aminoethyl) amino]-ethanol
H_2O	Water
CO_2	Carbon dioxide
SO_2	Sulphur dioxide
O_2	Oxygen
H_2S	Hydrogen sulphite
$NaHCO_3$	Sodium bicarbonate
ILs	Ionic liquids
TSILs	Task-specific ionic liquids
RTILs	Room temperature ionic liquids
CO_2BOLs	CO_2-binding organic liquids
COS	Carbonyl sulfide
[gua][OTf]	Guanidinium trifluoromethanesulfonate
[bmim][BF_4]	1-butyl-3-methylimidazolium tetrafluoroborate
[bmim][OTf]	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[bmim][PF_6]	1-butyl-3-methylimidazolium hexafluorophosphate
[bmim][NTf_2]	1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide

[emim][C$_2$N$_3$]	1-ethyl-3-methylimidazolium dicyanamide
[emim][NTf$_2$]	1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide
[emim][EtSO$_4$]	1-ethyl-3-methylimidazolium ethyl sulfate
[emim][OTf]	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
[emim][MDEGSO$_4$]	1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy) ethylsulfate
[N$_{4111}$][NTf$_2$]	*N*-butyltrimethylammonium bis[(trifluoromethyl)sulfonyl]imide
AAD	Absolute average deviation
MET	Measurement Equivalence-point Titration
ρ	Density of the system (g cm^{-3})
α_p	Coefficient of thermal expansion
η	Viscosity of the system (mPas)
η_∞	Viscosity at infinite temperature (mPas)
α_{CO2}	CO$_2$ loading (mol of CO$_2$/ total mol system)
	note: total mol system = mol (MDEA + [gua][OTf] + H$_2$O)
T	Temperature (K)
T_θ	Standard temperature (298 K)
P_{CO2}	Partial pressure of CO$_2$ (kPa)
P_T	Total pressure (kPa)
P_V	Vapor pressure (kPa)
R	Gas constant, 8.314 (kJ/ mol K)
E_a	Activation energy (kJ/ mol)
V_{HCl}	Volume of HCl needed to neutralize the basic species (mL)
V_{sample}	Volume of sample taken for analysis (mL)
V_{gc}	Volume of gas container (L)
V_{cell}	Volume cell (L)
V_{sol}	Volume solution (L)
$_i$	Initial condition
$_f$	Final condition
M	Molarity (mol dm^{-3})

[MDEA]$_t$	Total concentration of MDEA (mol dm^{-3})
n_{total}	Summation of moles of MDEA and/ or the other absorbents in the liquid phase
K$_{ov}$	Overall equilibrium constant
H$_{CO2}$	Henry's constant
x_{il}	Mole fraction of ionic liquid
x_{CO2}	Mole fraction of CO_2
ω	Angular velocity of spindle (rad/ sec)
R_c	Radius of container (cm)
R_b	Radius of spindle (cm)
L	Effective length of spindle (cm)
ml	Millilitre
K	Kelvin
kJ	Kilojoule
kg	Kilogram
m	Meter
cm	Centimeter
MPa	Megapascal
kPa	Kilopascal
M	Mol dm^{-3}
mPas	Millipascal
ppm	Parts per million
cP	Centipoise
h	Planck constant, $6.62606896 \times 10^{-34}$ J^{-1}
Y^E	Excess Gibbs energy of activation for viscosity flow
N_A	Avogadro's number, $6.022\ 141\ 99 \times 10^{23}$
γ	Thermal pressure coefficient
V^E	Excess molar volume