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Submitted by

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for the fulfilment of the requirements for the degree of

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Date : July, 2009

Dedicated

to

the great affection and love of my

Father (Muhammad Nawaz), Mother and Son (Muhammad Usman)

UNIVERSITI TEKNOLOGI PETRONAS

Thermophysical Properties and Solubility of CO_2/CH_4 in Aqueous Alkanolamine Solutions and Ionic Liquids

by

Ayyaz Muhammad

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Chemical Engineering Department

BANDAR SERI ISKANDAR,
PERAK

JULY, 2009

DECLARATION

I 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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ABSTRACT

Natural gas is the most useful and vital source of energy which could be considered as one of the cleanest and safest fossil fuel as compared to oil and coal. Regardless of the natural gas (NG) importance, it is usually contaminated with acid gases such as carbon dioxide (CO_2). The percentage of CO_2 in natural gas varies widely depending on the geological locations of gas fields. In some of the Malaysian gas fields in Peninsular and Sarawak, the average amount of CO_2 in natural gas has been found as high as 46 and 72 % respectively (Darman and Harun, 2006). The presence high CO_2 contents in NG decreases its heating value and also create corrosion and blockage problems during transmission. In many industrial applications, the selective separation of gas from mixture is usually performed by absorption process using glycol ethers and aqueous solutions of monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA) etc. Most recently, ionic liquids (ILs) have been introduced as novel solvents with unique properties such as negligible vapor pressure, high thermal stability and high gases selective solubility. The solvent characteristics play an extremely important role in the separation of gases at operating conditions of the absorption unit. The solubility measurements of gases in potential solvents are essential for generating reliable gas liquid equilibrium (GLE) data which provide basic information for the design and development of industrial absorption processes.

In the present work, a fundamental study is carried out to systematically investigate the potential application of imidazolium based ILs for bulk removal of CO_2 from NG to replace the existing alkanolamine solutions. For this purpose, initially thermophysical properties (density, isobaric thermal expansion coefficients, viscosity, surface tension, and refractive index) of aqueous MDEA/PZ solutions and ILs were measured and correlated. Thermal stability of all the studied solvents was also explored using a thermogravimetric analyzer (TGA). The density and viscosity values for all the studied ILs were found to be higher than all the studied amine solutions. The effect of pressure on densities of ILs was found to be insignificant up to 100 bar. The IL: $[C_6mim][PF_6]$ was

found to be highly viscous as compared to other studied ILs i.e., 431 mPa.s at 303.2 K. The surface tension of solvents was found to be in decreasing order of (PZ + water), (MDEA + PZ + water), (MDEA + water) and ionic liquids. The studied imidazolium based ILs showed very high thermal stability with their onset temperature values reaches three times higher than the amine solutions. A theoretical understanding has been proposed to develop a relationship between solvent physical properties and solubility behavior which is based on the experimental conclusions of physical properties of solvents.

The solubility measurements for pure CO_2 and its binary mixtures with CH_4 are performed in all the studied solvents at temperature range of (303.15 to 333.15) K and pressure up to 90 bar. The solubility experiments were performed in a specially designed high pressure gas solubility cell with auto data logging and acquisition system and an online gas chromatograph (GC). The CO_2 solubility in 4 molal and 8 molal aqueous MDEA solutions reached to 5.138 (moles.kg^{-1}) and 9.132 (moles.kg^{-1}) at P ≈ 54 bar and at T = 303.15 K. The CO_2 solubility in ILs with different anions was found to be in decreasing order of [C_6mim][Tf_2N], [C_6mim][PF_6] and [C_6mim][BF_4] at P ≈ 60 bar and at temperature range from 303.15 K to 333.15 K. The effect of ILs' anion appeared to play the most significant role in determining the CO_2 solubility as the IL with [Tf_2N] anion showed highest CO_2 solubility (5.483 moles.kg^{-1}) than [PF_6] and [BF_4] i.e., 3.428 and 3.872 (moles.kg^{-1}) respectively. The solubility measurements for CO_2/Methane in fresh solvents and recycled ILs were performed at exploration conditions of upstream NG with a perspective to explore potential capabilities of ILs to replace alkanolamines. The amount of CO_2 dissolved in recycled ILs was found to be similar to that obtained for ILs with maximum deviation of 6.8% obtained in case [C_6mim][PF_6]. The solubility of CO_2 in all the studied solvents significantly decreased due to presence of methane in gaseous mixtures in comparison to its solubility as pure carbon dioxide. The gas liquid equilibrium (GLE) data is correlated with an extended Henry's law constant using Peng-Robinson Equation of State (PR-EOS) approach and other important thermodynamic parameters (Enthalpy, Gibbs free energy and Entropy) of solutions were investigated.

ABSTRAK

Gas asli adalah sumber tenaga terpenting yang juga diambilkira sebagai salah satu sumber tenaga yang paling bersih dan selamat untuk digunakan berbanding minyak dan arang batu. Walau bagaimanapun, sumber gas asli ini selalu dicemari oleh kebanyakan gas asid seperti karbon dioksida (CO_2). Peratusan karbon dioksida yang terkandung di dalam gas asli adalah berbeza-beza kerana ia bergantung kepada keadaan bentuk muka bumi sesebuah lokasi lapangan gas. Kebanyakan lapangan gas di Malaysia terutama di Semenanjung dan Sarawak, purata kandungan karbon dioksida yang tinggi dalam gas asli adalah masing-masing 46 and 72% (Darman and Harun, 2006). Kehadiran kandungan karbon dioksida yang tinggi dalam gas asli menyebabkan nilai untuk pemanasan berkurang tetapi juga menyebabkan masalah hakisan dan sekatan semasa peralihan gas asli. Di kebanyakan aplikasi industri, pengasingan terpilih gas daripada campuran boleh dilakukan dengan kaedah penyerapan yang disertai dengan penggunaan 'glycol ether' dan larutan cecair 'monoethanolamine' (MEA), 'diethanolamine' (DEA), '*N*-methyldiethanolamine' (MDEA) dan sebagainya. Terkini, cecair ionik (ILs) telah diperkenalkan sebagai pelarut yang baru yang mempunyai sifat-sifat unik seperti tekanan wap yang boleh diabaikan, kestabilan termal yang tinggi, dan kelarutan gas terpilih yang tinggi. Sifat pelarut memainkan peranan yang penting dalam pengasingan pelbagai gas ketika keadaan operasi sesebuah unit penyerapan. Pengukuran kelarutan gas untuk pelarut yang berpotensi adalah penting untuk menghasilkan data keseimbangan gas-cecair (GLE) yang seterusnya menyediakan asas dan maklumat untuk reka bentuk dan perkembangan kaedah penyerapan di dalam industry.

Di dalam kajian semasa, satu kajian asas telah dilakukan secara sistematik untuk menyelidik potensi aplikasi 'imidazolium' berasaskan ILs untuk pembuangan karbon dioksida secara pukal daripada gas asli bagi menggantikan larutan 'alkanolamine'. Bagi tujuan ini, sifat termofisik (ketumpatan, pekali pengembangan termal isobarik, kelikatan, tekanan permukaan , dan indeks pembiasan) cairan larutan MDEA/PZ dan ILs telah ditentukurkan dan dihubungkaitkan pada mulanya. Kestabilan termal bagi semua pelarut

yang dikaji juga diselidik dengan menggunakan 'thermogravimetric analyzer' (TGA). Didapati nilai ketumpatan dan kelikatan untuk semua ILs yang telah dikaji lebih tinggi daripada larutan amine yang telah dikaji. Kesan tekanan terhadap ketumpatan ILs didapati tidak signifikasi sehingga ke 100 bar. IL: [C_6mim][PF_6] didapati lebih likat berbanding lain-lain ILs yang dikaji, iaitu, 431 mPa.s pada 303.2 K. Tekanan permukaan pelarut didapati dalam urutan menurun untuk (PZ + air), (MDEA + PZ + air), (MDEA + air) dan cecair ionik. Imidazolium, berasaskan ILs, yang dikaji telah menunjukkan stabiliti termal yang sangat tinggi dengan nilai suhu permulaan mencecah tiga kali ganda lebih tinggi daripada larutan amine. Satu teori pemahaman dicadangkan untuk membina satu hubungan antara sifat fizikal pelarut dengan tabiat kelarutan berdasarkan kesimpulan daripada eksperimen sifat-sifat fizikal bagi pelarut.

Pengukuran kelarutan untuk karbon diosida tulen dan dwi-campurannya dengan CH_4 telah dijalankan dalam larutan yang dikaji pada suhu antara (303.15 sehingga 333.15) K dan tekanan sehingga ke 90 bar. Eksperimen kelarutan telah dijalankan di mana ia direka secara khusus tekanan tinggi sel kelarutan gas bersama 'auto data logging' dan sistem perolehan serta 'gas chromatograph' (GC) secara talian. Kelarutan CO_2 dalam 4 molal dan 8 molal larutan akuas MDEA mencecah sehingga 5.138 (moles.kg^{-1}) dan 9.132 (moles.kg^{-1}) pada P ≈ 54 bar dan pada T = 303.15 K. Didapati kelarutan CO_2 dalam ILs dengan anion yang berbeza adalah dalam urutan menurun bagi [C_6mim][Tf_2N], [C_6mim][PF_6] dan [C_6mim][BF_4] pada P ≈ 60 bar dan pada suhu antara 303.15 K to 333.15 K. Kesan anion ILs merupakan peranan yang penting dalam menentukan kelarutan CO_2 kerana IL bersama anion [Tf_2N] menunjukkan kelarutan CO_2 yang tertinggi berbanding [PF_6] dan [BF_4] iaitu masing-masing 3.428 dan 3.872 (moles.kg^{-1}). Pengukuran kelarutan untuk CO_2/metana di dalam pelarut segar dan ILs kitar semula telah dijalankan pada keadaan explorasi 'upstream NG' dengan perspektif untuk menyelidik potensi keupayaan ILs bagi menggantikan alkanolamine. Jumlah CO_2 yang dilarutkan dalam ILs kitar semula didapati menyerupai jumlah yang diperoleh bagi ILs dengan pesongan maksimum 6.8% dalam kes [C_6mim][PF_6]. Kelarutan CO_2 di dalam semua pelarut yang dikaji menurun dengan mendadak disebabkan kehadiran metana di

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LIST OF ABBREVIATIONS

MDEA	*N*-Methyldiethanolamine
PZ	Piperazine
ILs	Ionic liquids
RTILs	Room temperature ionic liquids
MILL	Malaysian ionic liquid laboratories
CO_2	Carbon dioxide
CH_4	Methane
LTHP	Low temperature and high pressure
GLE	Gas-liquid equilibrium
SC	Solubility cell
TGA	Thermaogravimetric analyzer
SD	Standard deviations
AAD	Average abasolute deviations
EOS	Equation of State

LIST OF SYMBOLS

ρ	Density (kg.cm^{-3})
η	Viscosity (m.Pa.s)
σ	Surface tension (m.N.m^{-1})
$\alpha_{\mathbf{p}}$	Isobaric thermal expansion coefficients
nD	refractive index
$k_{H,CO_2}(T)$	Henry's law constant
$f_{CO_2}(T,P)$	Fugacity of CO_2 at equilibrium temperature and pressure
$\phi_{CO_2}(T,P)$	Fugacity coefficient of CO_2 at equilibrium temperature and pressure
m_{CO_2}	Solubility of CO_2 on molality scale (mole.kg^{-1})