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Solubilities of CO_2 in aqueous *N*-methyldiethanolamine and guanidinium trifluoromethanesulfonate ionic liquid systems at elevated pressures

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ABSTRACT

In this work, the solubility of CO_2 in aqueous blended systems of *N*-methyldiethanolamine (MDEA) and guanidinium trifluoromethanesulfonate ($[gua]^+[OTf]^-$) have been carried out. The solubilities were measured at temperature 303.2 K, 323.2 K and 333.2 K, over CO_2 partial pressure ranging from 500 to 3000 kPa. All data were reported as loading capacity (mol CO_2/total mol) as a function of partial pressure of CO_2 at the corresponding temperature. It has been found that the aqueous $[gua]^+[OTf]^-$ ionic liquid gave significantly higher solubility, up to 1.63 mol CO_2/total mol, as compared to other pure ionic liquids such as $[bmim]^+[BF_4]^-$, $[emim]^+[OTf]^-$ and $[emim]^+[C_2N_3]^-$ which recorded at 323.2 K and 3000 kPa. However, the addition of $[gua]^+[OTf]^-$ ionic liquid to aqueous MDEA gave a slight decreased on solubility. Correlations of solubility as a function of partial pressure and temperature were obtained with deviation of ±0.957%.

1. Introduction

Anthropogenic CO_2 emission, which has led to global climate change, has become an issue of severe concern. Numerous attempts are being taken to overcome this problem. CO_2 capture from large point sources, such as power plants, can be achieved by various approaches, namely; post-combustion capture, pre-combustion capture, oxy-combustion, gas phase separation, absorption into liquid, adsorption on solid and membrane systems. In pre-combustion CO_2 capture, the technology is inherently deals with high-pressure condition [1,2]. The related equilibria data are in high demand as proven by the 1013 journals found in literature within a decade (1988–1999) [3,4], followed by the continuously increasing commentary on these high-pressure systems.

The removal of CO_2 from gas stream is commonly carried out by absorption in a solvent, either chemical or physical. The selective CO_2 loading at high-pressure are influenced by an array of solvents and favored by high pressure and low temperature [5]. Various research groups have studied a number of solvents in these recent years. Selexol, rectisol, propylene carbonate, dimethyl ether of polyethylene glycol (MPE), *N*-methyl-2-pyrrolidone (NMP), methanol, tributyl phosphate and methylcyanoacetate are examples of physical solvents that has been used commercially [6]. Apart from that, ionic liquids, such as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, 1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate, and (tri-iso-butyl(methyl)phosphonium tosylate + water) systems [7,8] have also been studied as potential physical solvents. The chief advantages of a physical solvent are the capacity of the solvent, which is not restricted by the stoichiometry and necessitate less energy for the regeneration process. However, these solvents may have a few drawbacks such as high sensitivity to acid gas partial pressure and difficulty to meet gas specifications [9].

On the other hand, chemical solvents are defined as solvents in which acid gases react to form a complex. They are typically aqueous alkanolamine solutions, i.e., methylethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), diisopropanolamine (DIPA), diglycolamine (DGA) [10–17], diamine 2-[(2-aminoethyl)amino]-ethanol (AEEA) [18] and also CO_2-binding organic liquids (CO_2BOLs) [19]. These types of solvents carry the advantage of being proficient in removing the acid gases to ppm levels, even at low pressures. Although amines have been used for many years, particularly in the removal of acid gases from natural gas, there are still several drawbacks, which need to be improved [20].

Hence, mixed solvents are an attempt to merge the separate advantages of chemical and physical solvents for the hybrid process [21,22]. Depending upon the solvent–amine combination, it is believed that nearly complete removal of CO_2, H_2S and COS is possible. Presently, sulfinol, which consists of a combination of sul-

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folane (physical solvent) and DIPA or MDEA (chemical solvent), is one of the more commonly used processes. Generally, all the solvents possess hydroxyl and amino groups. It can be contemplated that the hydroxyl group serves to reduce the vapor pressure and increase the water solubility, while the amino group offer the necessary alkalinity in water solutions to cause the absorption of acidic gases [23]. In addition, from the engineering point of view, optimum viscosity plays chief role in stirring, mixing and pumping operation. The viscosity of many ionic liquids which affected the transport properties such as diffusion, relatively differs at least one to three orders of magnitude higher, compared to conventional solvents. The range reported so far is from 66 to 1110 cP at 293–298 K. Therefore, in one embodiment of the mixed solvent is to lower the viscosity while enhancing the performance of the systems [24–30].

Moreover, since ionic liquids are physical solvents, little heat is required for regeneration. Featuring good thermal stability, trifling vapor pressure, it is believed to be a good potential solvent. In the wake of this potential, the purpose of the present work is to explore a new solvent for acid gas removal. A few systems of these physical and chemical solvents were designated and compared. MDEA was chosen as the chemical solvent as its lower vapor pressure and less corrosive among others [31–36]. Meanwhile, the amine-functionalized ionic liquid, [gua]$^+$[OTf]$^-$ was granted to perform as the physical solvent. Furthermore, the cation of this new task-specific ionic liquid consists of a guanidinium ion to which a tertiary amine moiety is covalently tethered.

2. Material and methods

2.1. Material

Purified CO_2 (purity ≥ 99.995%) was obtained from Malaysian Oxygen Berhad (MOX). Both MDEA (purity ≥ 98.5%) and ionic liquid, [gua]$^+$[OTf]$^-$ (purity ≥ 98%) were purchased from Merck. Fig. 1 shows the chemical structures of MDEA and [gua]$^+$[OTf]$^-$. All weight measurements were done using an analytical balance with an accuracy of ±0.1 mg.

Four systems were prepared in this work. They are denoted as 4M0G, 4M1G, 1M0G and 0M1G. The compositions of the systems are tabulated in Table 1.

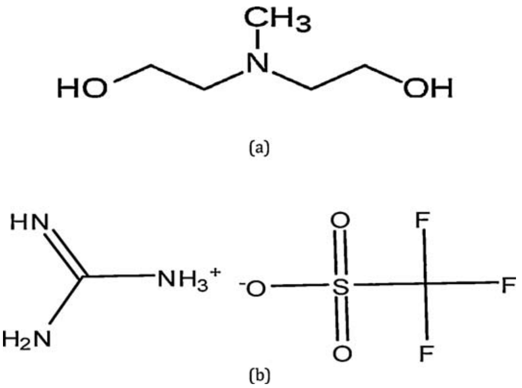

Fig. 1. The chemical structures of (a) *N*-methyldiethanolamine (MDEA) (b) guanidinium trifluoromethanesulfonate ([gua]$^+$[OTf]$^-$).

Table 1
Composition of the studied systems.

Sample	Concentration of MDEA/mol/dm^{-3}	Concentration of [gua]$^+$[OTf]$^-$/mol/dm^{-3}
4M0G	4.012 ± 0.002	0
4M1G	4.008 ± 0.002	1.005 ± 0.002
1M0G	1.003 ± 0.002	0
0M1G	0	1.006 ± 0.002

2.2. Methods

Fig. 2 illustrates a schematic diagram of the batch reactor cell, which has a welded stirrer assemble, a thermocouple, an inlet gas tube and air vent tube. Both integrated reactor with a thermostated heater and thermocouple had the accuracy within ±0.1 K. Fig. 3 shows a full schematic process flow diagram of the high-pressure system. Operation was initially started by purging the air out from the gas reservoir by sufficiently flow CO_2 through out the system. The gas reservoir tank was loaded with purified CO_2 from the storage tank before it was heated and pressurized to the required condition. A known volume of fresh sample was filled in the thermostated high-pressure reactor cell prior sealed.

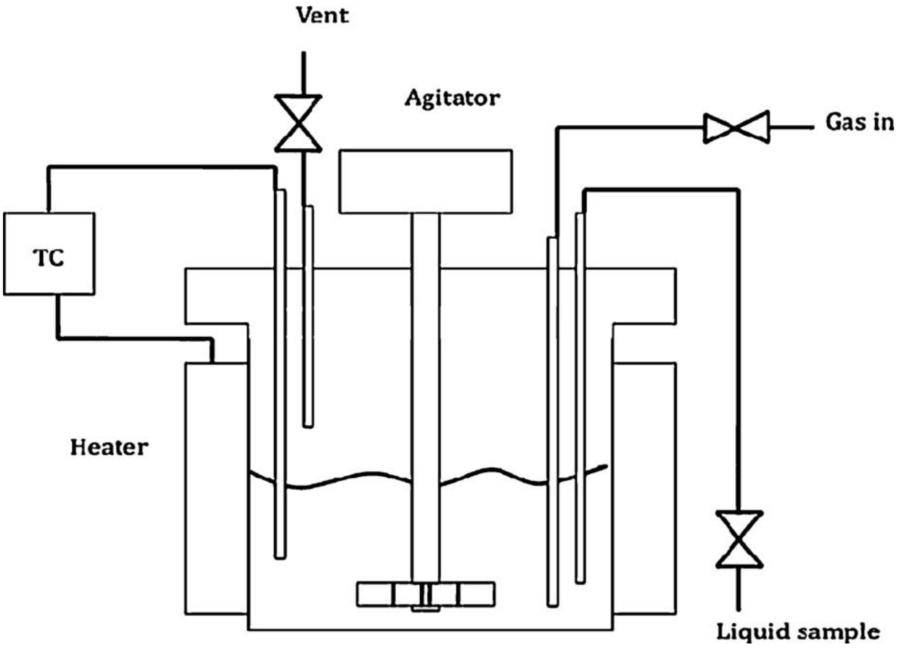

Fig. 2. A diagram of batch reactor cell.