



CO₂ SOLUBILITY IN AQUEOUS MONOETHANOLAMINE WITH 1-ETHYL-3-METHYLIMIDAZOLIUM TETRAFLUOROBORATE

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Abstract

Aqueous monoethanolamine (MEA) solution (15 wt%) was mixed with 5, 10, 15 wt% ionic liquid namely, 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄]). CO₂ solubility in aq. MEA and aq. MEA-IL mixtures was measured experimentally at $T = 298.15$ K and over a pressure range of 100 to 3000 kPa. The addition of IL in the aq. MEA solutions affected its solubility. The solubility of all the mixtures increased with increase in pressure.

Keywords: CO₂ solubility, monoethanolamine, 1-ethyl-3-methylimidazolium tetrafluoroborate, hybrid solvent

1. Introduction

Carbon dioxide (CO₂) is a major green house gas causing environmental pollution and global warming. Its average concentration is more than 350ppm (upper limit for atmospheric CO₂) in most parts of the world [1]. Extensive burning of fossil fuel (due to its high demand) is a major contributing factor for enhanced CO₂ emissions [2]. There is a major shift among the plants operating on conventional fuel to comparatively clean fuel like natural gas. The increasing demand for natural gas calls for the exploitation of its sour sources. CO₂ removal from natural gas increases its calorific value and hence helps it to meet the pipeline and pricing specifications [3]. Most of the CO₂ capture processes are based on amine solvents. Though amine solvents are environmental unfriendly yet these are extensively used due to their reactivity and effectiveness. Ionic liquids (ILs) are envisaged as alternative green solvents and have been utilized by many researchers for CO₂ capture. Low vapor pressure and high thermal stability are some of IL's favorable properties. However their high viscosity and high price limit their large scale industrial usage. Recently hybrid solvents (amine + ILs) for CO₂ capture have drawn attention of researchers. Such mixtures are aimed to possess the environmentally benign characteristics of ILs and the fast reactivity of amines [4-5]. Many researchers [4, 6-12] have reported CO₂ solubility data in IL-amine mixtures since this idea was presented in 2008. Plenty of room is available for such mixtures to be utilized for CO₂ capture. A lot of mixtures can be prepared due to the enormous number of reported ILs for CO₂ removal.

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Targeted IL can be mixed with amine solvent to result in a number of hybrid mixtures. These mixtures can later be evaluated in terms of their capability for CO₂ absorption. The present study aims to utilize aqueous mixtures of IL; 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄]) with monoethanolamine (MEA) for CO₂ capture. Aqueous amine (15wt% MEA) solution was mixed with IL (5-15 wt%) and CO₂ solubility was measured in these mixtures at $T = 298.15$ K and pressures up to 3000 kPa.

2. Materials and Methods

2.1. Materials

Ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (purity >98.99% HPLC area) and monoethanolamine (purity 99%) were supplied by Sigma-Aldrich, Malaysia, Sdn. Bhd. Water contents of IL were estimated by using Coulometer Karl Fischer titrator DL-39 (Mettler Toledo) with Hydranal Coulomat AG reagent (Riedel-d-Haen). The measurements were made in triplicate and average value is reported here. The estimated water contents of the IL were 293ppm. The water used for making aqueous solutions was doubly distilled and de-ionized. The samples were prepared by using an analytical balance (model AS120S, Mettler Toledo) with a precision of 0.0001g. Samples were kept in glass vials with PTFE septum.

2.2. Gasses

Purified Carbon dioxide and Nitrogen used in this study were purchased from Malaysian Oxygen Berhad. Carbon dioxide was supplied with a stated purity of >99.9% and other contents included moisture <10vpm and hydrocarbon <1vpm. Nitrogen was having purity >99.9999%.

2.3. Methods and Apparatus

CO₂ solubility in the aqueous mixtures was estimated by using pressure drop method. High pressure solubility cell SOLTEQ (Model BP 22) was used in this study. The schematic diagram of the apparatus is shown in Figure 1. Major components of solubility cell include the storage vessel for the gas and the absorption cell. Absorption cell and storage vessel were jacketed to maintain the temperature at the desired value during the course of experimentation. Air driven gas booster pump (Haskel, model AG 15) was used to build a desirable pressure in storage vessel. Gas was transferred at desired pressure from the storage vessel to the absorption cell. Absorption cell was connection to gas evacuation system, which establishes vacuum in it prior to the dosing of the sample. Evacuation system consists of turbo molecular vacuum pump (Pfeiffer, model TSH 071 E). Reciprocating metering pump (Eldex Laboratories Inc. USA) was used to pump in the samples into the absorption cell. Prior to commence each experiment the absorption cell was thoroughly cleaned by utilizing solvents like methanol, acetone etc. After that the cell was purged with Nitrogen gas to make it dry. Amount of absorbed CO₂ was estimated by using the following set of equations [13]. CO₂ (moles) transferred from the storage vessel to the absorption cell was calculated by using the equation:

$$n_{CO_2} = \frac{V_T}{RT} \left(\frac{P_1}{z_1} - \frac{P_2}{z_2} \right) \quad (1)$$

where V_T is the volume of the mixing vessel and z_1 and z_2 are the compressibility factors corresponding to the initial (P_1) and final (P_2) pressure of the mixing vessel before and after transferring CO_2 and T is the temperature of the mixing vessel. Equilibrium pressure was calculated by using the equation:

$$P_{\text{CO}_2} = P_T - P_v \quad (2)$$

where P_T denotes the total pressure (equilibrium pressure), P_v represents the vapor pressure of the liquid samples which can be neglected in the case of pure IL and amine and subsequently of their mixtures also as the IL and MEA exist under negligible vapor pressure for the studied temperature [14-15].

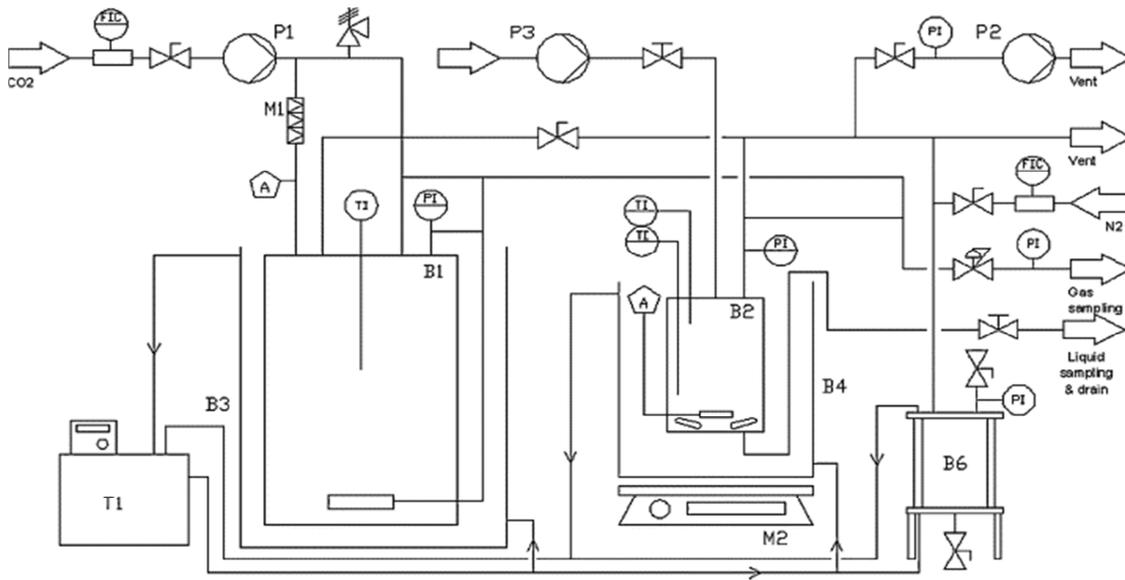


Figure 1. Schematic diagram of SOLTEQ-BP22 high pressure solubility cell used in the present study. B1, mixing cell; B2, equilibrium cell; B3, heating jacket for B1; B4, heating jacket for B2; B6, liquid degassing unit; M1, static mixer; M2, magnetic stirrer; T1, thermostat heating bath; P1, gas booster; P2, vacuum pump; P3, liquid pump.

Moles of the remaining (unabsorbed) CO_2 in the gas phase were calculated by using the following equation:

$$n_{\text{CO}_2}^g = \frac{V_g P_{\text{CO}_2}}{z_{\text{CO}_2} RT} \quad (3)$$

where V_g is the gas-phase volume of the equilibrium cell, z_{CO_2} is the compressibility factor at P_{CO_2} , T is the temperature inside the cell. The moles of the CO_2 dissolved in the liquid phase were then determined by using the equation:

$$n_{\text{CO}_2}^1 = n_{\text{CO}_2} - n_{\text{CO}_2}^g \quad (4)$$

The CO_2 absorbed was expressed in terms of mole fraction by using Eq. 5 (for the case of pure liquids), Eq. 6 (for the case of binary mixtures) and Eq. 7 (for the case of ternary mixtures).

$$x_{CO_2} = \frac{n_{CO_2}^1}{n_{liq} + n_{CO_2}^1} \quad (5)$$

$$x_{CO_2} = \frac{n_{CO_2}^1}{n_{H_2O} + n_{MEA} + n_{CO_2}^1} \quad (6)$$

$$x_{CO_2} = \frac{x_{CO_2}^1}{n_{IL} + n_{amine} + n_{CO_2}^1 + n_{H_2O}} \quad (7)$$

Compressibility factors were estimated by using equations of state (EOS) including Van der Waals, Redlich Kwong (RK), Soave Redlich Kwong (SRK), Peng Robinson (PR). A computer program written by chemSOF was used for this study to estimate compressibility factors by using different EOS.

3. Results and Discussion

Aqueous monoethanolamine (15wt%) solution was mixed with 5, 10, 15 wt% ionic liquid namely 1-ethyl-3-methylimidazolium tetrafluoroborate. These four mixtures were later examined in terms of CO₂ solubility experimentally by using pressure drop method at $T = 298.15$ K and pressures ≥ 100 kPa to ≤ 3000 kPa. Effect of the presence of IL in the aqueous amine solution at different concentrations was monitored. The experimental CO₂ solubility results in the aqueous IL-amine systems under study are listed in Table 1 and graphically illustrated in Figure 2. It can be seen that aq. MEA solutions showed highest solubility among all the mixtures. The addition of IL in the aq. amine solutions decreased its solubility. The 5 % IL solution showed 1.03731 times lower values of solubility in comparison to aq. MEA solution. Though the decrement is not significant yet it cannot be neglected. Similarly 10% and 15% IL mixtures showed lower values of CO₂ solubility as compared to aqueous amine solution. It can be inferred that the addition of IL to the aqueous amine solution has not proved fruitful in terms of CO₂ solubility. Even the slightest amount of IL present in the aqueous amine solutions decreased its solubility. However interestingly it was observed that the presence of IL in the aq. amine solution increased the initial absorption rate of the solvents. This is due to the fact that imidazolium based ILs have proven their capability for selective physical absorption of CO₂. Initially the chemical and physical absorption of CO₂ simultaneously took place which resulted in the enhanced absorption rate. Similar trends were noted by the Ahmady et. al. [8] while examining the mixtures of aqueous *N*-methyldiethanolamine (MDEA) with IL (1-butyl-3-methylimidazolium tetrafluoroborate) for CO₂ absorption. They made these observations at $P = < 110$ kPa. The present study carried out the higher temperature range shows that the decrease in CO₂ solubility by the presence of IL is independent of pressure range. Though pressure is increased trend cannot be reversed. Physical absorption of the ILs cannot supersede the chemical absorption of amines. It is noteworthy to mention that physical absorption of CO₂ in the ILs increases with increase in pressure. The decrease in CO₂ solubility in all aq.MEA-IL mixtures, due to the addition of IL can be explained in terms of the increment in the concentration of pure amine. Water content of the

aq.MEA solution decreased by the addition of IL. As their addition was carried out at the expense of the water part of the aqueous solution.

Table 1. CO₂ solubility data in the aq. MEA (15%) and aq. IL amine mixtures.

p/kPa	x_{CO_2}	p/kPa	x_{CO_2}	p/kPa	x_{CO_2}	p/kPa	x_{CO_2}
aq. MEA		5% IL		10% IL		15% IL	
155	0.0285	149	0.0273	152	0.0254	148	0.0235
349	0.0301	344	0.0289	347	0.0270	343	0.0251
637	0.0327	628	0.0316	623	0.0295	626	0.0275
1027	0.0357	1031	0.0345	1025	0.0325	1033	0.0305
1532	0.0385	1527	0.0371	1529	0.0352	1531	0.0331
2028	0.0401	2021	0.0387	2023	0.0371	2054	0.0351
2521	0.0412	2513	0.0399	2523	0.0382	2543	0.0362
2955	0.0421	2942	0.0406	2954	0.0387	2943	0.0367

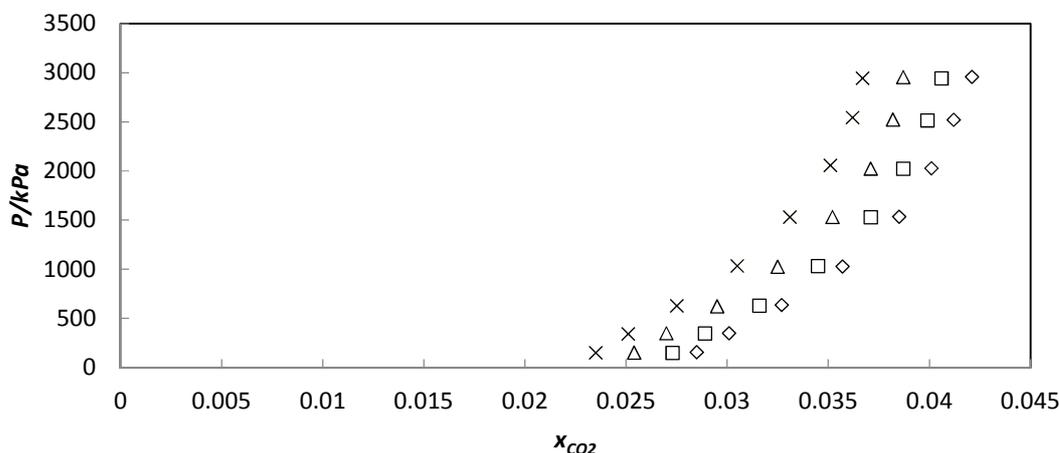


Figure 2. CO₂ solubility in aqueous IL + amine mixtures: Aqueous amine {15wt% MEA} (◇), 5wt% [emim][BF₄] (□), 10wt% [emim][BF₄] (Δ), 15wt% [emim][BF₄] (×)

It is well established that as concentration of pure amine solvents increases in the aqueous solutions the CO₂ solubility decreases subsequently.

4. Conclusions

Ionic liquid namely 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄]) was mixed with aqueous monoethanolamine (MEA) (15wt% aq. solution) at different wt % (5, 10, 15). Aqueous MEA and the aq. amine-IL mixtures were evaluated in terms of CO₂ solubility experimentally by using pressure drop method at $T = 298.15$ K and pressures (≥ 100 kPa - ≥ 3000 kPa). It was observed that the CO₂ solubility in all the solvents increased with increase in pressure. However the addition of IL in the aqueous amine solution did not prove beneficial for the former in term of CO₂ absorption. The aq. amine solution suffered loss in CO₂ solubility by the addition of IL at all

concentrations. Though initially fast absorption rate in aq.amine-IL mixtures was observed in comparison to aq.amine solution.

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