

Solubility of Carbon Dioxide in Five Promising Ionic Liquids

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According to many environmental aspects, the use of ionic liquids as potential solvents for CO₂ capture and natural gas sweetening processes has gained much attention from many researchers in recent years. This research experimentally determines the solubility of CO₂ in five ionic liquids: triethylsulfonium bis(trifluoromethylsulfonyl)imide ([S₂₂₂][Tf₂N]), diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ([deme][Tf₂N]), 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([pmim][Tf₂N]), 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([amim][Tf₂N]), and 1-butyl-4-methylpyridinium tetrafluoroborate ([4mbp][BF₄]) at (313.15, 323.15 and 333.15 K) and pressures up to 20 bar using a gravimetric microbalance. The solubility of CO₂ diminished in the following sequence: [deme][Tf₂N] > [pmim][Tf₂N] > [amim][Tf₂N] > [S₂₂₂][Tf₂N] > [4mbp][BF₄]. The solubility of CO₂ in these ionic liquids increased as temperature decreased. Four studied ionic liquids, [deme][Tf₂N], [pmim][Tf₂N], [amim][Tf₂N], [S₂₂₂][Tf₂N] are deemed promising because of high CO₂ solubility with a physical absorption when compared to [hmim][Tf₂N]. These physical solvents have lower solubility than [bmim][Ac] which exhibited a strong chemical absorption and the reported formation of a chemical complex. Henry's law constants for the investigated ionic liquids were derived.

1. Introduction

Carbon dioxide (CO₂) is one of the most dominant green house gases (GHGs) present in Earth's atmosphere. It is known to act as a natural blanket to make the whole atmosphere and the surface of the earth adequately warm for human beings and creatures living on earth. The origin of CO₂ is derived from burning of organic substances especially fossil fuels, and has remained consistent for the last few thousand years. Since the beginning of industrialization, global environmental problems concerning the emissions of GHGs have become a critical issue due to the steady rise in the amount of anthropogenic CO₂ in the atmosphere (Goldemberg, 2012). CO₂ has not only originated from fossil fuel-based power generation, but another significant source is also derived from produced natural gas found at the wellhead (Mortazavi-Manesh et al., 2011). Coupled with the feasibility of the utilization of captured CO₂ in enhanced oil recovery (EOR), many research studies are underway in order to develop more economical and environmentally benign novel technologies for efficient capture and sequestration from large CO₂ emission sources. Currently, the most commercially advanced CO₂ capture technology uses aqueous amine solutions, such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA), as chemical absorbents. These amine solutions are regarded as the most feasible option due to high CO₂ reactivity, low cost and high CO₂ absorption capacity. However, CO₂ absorption by amines presents some drawbacks such as intensive energy consumption during regeneration, equipment corrosion, solvent degradation and vaporization losses (Ma'mun et al., 2005). While more energy- and cost-efficient amine solution technologies are perpetually being investigated, the discovery of more innovative solvents for CO₂ capture is of vital importance. Among the emerging technologies for CO₂ capture, ionic liquids are regarded as more environmentally friendly and energy-efficient CO₂ capture technology.

Ionic liquids are a category of organic salts that remain liquid at or near room temperature. In general, the structure of ionic liquids consists of a bulky asymmetric organic cation and either an inorganic or organic anion, making them low melting points (Marsh et al., 2004). They have a number of advantages, as determined by their unique physicochemical properties, such as negligibly low vapour pressure, high

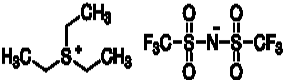
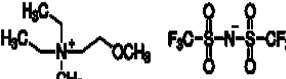
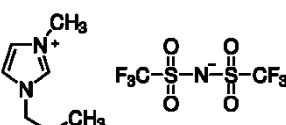
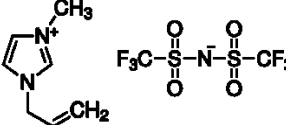
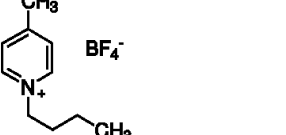
thermal stability, and structural tuneability make ionic liquids environmentally benign and appropriate for gas separation without solvent loss or contamination of vapour phase as well as being able to be tailored for specific applications. Nonetheless, for some, the high viscosity of ionic liquids is regarded as a very important drawback especially during CO₂ absorption, leading to a reduction of overall mass transfer rate and an increment in power requirement for pumping and mixing (Carvajal et al., 2012). Accordingly, the understanding of the solubility of gases in the ionic liquid phase and the selection of low-viscosity ionic liquids are prerequisites to their selection as potential solvents for CO₂ capture. In this research, the solubilities of CO₂ in five novel ionic liquids: triethylsulfonium bis(trifluoromethylsulfonyl)imide ([S₂₂₂][Tf₂N]), diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethyl sulfonyl)imide ([deme][Tf₂N]), 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([pmim][Tf₂N]), 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([amim][Tf₂N]), and 1-butyl-4-methylpyridinium tetrafluoroborate ([4mbp][BF₄]) were measured using a gravimetric microbalance (IGA-003). Our experimental CO₂ solubility data in the investigated ionic liquids were compared to data published in the literature for other ionic liquids. Henry's law constants for the ionic liquid + CO₂ systems studied were also reported.

2. Materials and methods

2.1 Materials

Ionic liquid samples were ordered from Sigma-Aldrich Ltd. Table 1 lists their names, abbreviations, chemical structures, purities, and CAS numbers. Carbon dioxide (CO₂) as research grade was purchased from Praxair Products Inc. with a purity of 99.99 %.

Table 1: Ionic liquids investigated in this work

Ionic liquids	Abbreviation	Chemical structure	Purity	CAS Number
Triethylsulfonium bis(trifluoromethylsulfonyl) imide	[S ₂₂₂][Tf ₂ N]		≥99.0 % (NMR)	321746-49-0
Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl) imide	[deme][Tf ₂ N]		≥98.5 % (T)	464927-84-2
1-Propyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide	[pmim][Tf ₂ N]		≥98.0 % (H-NMR)	216299-72-8
1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl) Imide	[amim][Tf ₂ N]		≥98.5 % (HPLC)	655249-87-9
1-Butyl-4-methylpyridinium tetrafluoroborate	[4mbp][BF ₄]		≥97.0 % (T)	343952-33-0

2.2 Experimental set-up and procedures

Gas solubility measurements were performed using a gravimetric microbalance (Hiden Isochema Ltd, IGA-003). The microbalance is composed of a sample bucket containing the liquid and counter weight components inside a stainless steel pressure-vessel. The stainless steel (SS316N) reactor is able to operate up to 20 bar and 500 °C. In the experiment, approximately (65 to 75) mg of ionic liquid sample were loaded to the sample container and the reactor was installed. After waiting for stability, the thermostat was then attached to the reactor and the external water jacket was connected. The sample was dried and degassed by fully evacuating the reactor to 10 - 8 bar. While performing ultra-high vacuum, the sample was heated to approximately 70 - 75 °C for at least 10 h by the water jacket connected to a constant-temperature bath. The sample weight slowly decreased since trace amounts of water and other volatile solvents were removed. Once the sample weight had stabilized for at least 60 min, the sample dry weight

was recorded. All absorption measurements in this work were performed in a static mode. The sample temperature was measured with a thermocouple located inside the reactor next to the sample container. The water jacket maintained the set point temperature automatically. Three temperatures of 313.15, 323.15 and 333.15 K were set as isotherms. Once the temperature status showed that it reached the set point and the weight was stabilized after waiting for 1 - 3 h, several pressure levels up to 20 bar (0.1, 0.5, 1.0, 2.0, 4.0, 7.0, 9.0, 10.0, 11.0, 13.0, 15.0, 17.0, 19.0 bar) were used in the present work. To ensure sufficient time for gas-liquid equilibrium, the ionic liquid samples were maintained at set point for a minimum time of 2 h with maximum time-out of 4 h. The real-time processor was used to determine the end-point for each isotherm. The percent relaxation used as an end point for the real-time analysis was 99 %. The effect of buoyancy was taken into consideration for the evaluation of CO₂ solubility in the ionic liquids. Densities of ionic liquids at different temperatures were measured experimentally using an Anton Paar density meter (DMA 4500) since the buoyancy correction requires the density data of the ionic liquids.

3. Thermodynamic calculations

At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. An equivalent meaning of this statement is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid. According to Husson-Borg et al. (2003), Henry's law constant can be defined as:

$$H_{2,1}(p_2, T) \equiv \lim_{x_2 \rightarrow 0} \frac{f_2^L(p_2, T, x_2)}{x_2} \quad (1)$$

In this work, we define an ionic liquid as component 1 and CO₂ as component 2. Therefore, $f_2^L(p_2, T, x_2)$ is the fugacity of CO₂ dissolved in the ionic liquid phase, x_2 is the mole fraction of CO₂ in the liquid phase, p_2 is the partial pressure of CO₂, and T is the temperature. At equilibrium, the fugacities of each component in the liquid phase are equal to those in the vapour phase, which can be expressed as:

$$f_2^L(p_2, T, x_2) = f_2^V(p_2, T, y_2) = \phi_2(p_2, T, y_2) y_2 p_2 \quad (2)$$

where, $\phi_2(p_2, T, y_2)$ is the fugacity coefficient of CO₂. For the (ionic liquid + CO₂) system, the ionic liquid is considered to have negligible vapour pressure:

$$\phi_2(p_2, T, y_2) y_2 p_2 = \phi_2(p_2, T) p_2 \quad (3)$$

For very low concentrations of CO₂ in the ionic liquid, Henry's law constant can be expressed as:

$$H_{2,1}(p_2, T) = \lim_{x_2 \rightarrow 0} \frac{\phi_2(p_2, T) p_2}{x_2} \quad (4)$$

For an ideal system, knowing the fugacity of CO₂ in the ionic liquid phase equivalent to the fugacity of CO₂ in the CO₂ phase is able to approximate the gas phase fugacity as the gas phase pressure. The following form of Henry's law can be obtained:

$$p_2 = H_{2,1}(T) \cdot x_2 \quad (5)$$

In the ideal gas case, Henry's law constant is a linear relationship between the mole fraction of CO₂ in the ionic liquid and pressure, which can be calculated from the slope of the experimental solubility data of gas at low solute concentrations. In most cases, the CO₂ isotherms are not linear over the whole range of pressures. Therefore, the experimental CO₂ solubility data are fitted with a second order polynomial and the limiting slope as the pressure (or solubility) approaches zero was calculated (Anthony et al., 2005). In this research, to be more accurate, we calculated the fugacity of CO₂ using the SRK equation of state with quadratic mixing rules. At each temperature, Henry's law constant is found by fitting the data of the plot between the fugacity versus the mole fraction of CO₂ with a second order polynomial correlation. Considering the equilibrium conditions and infinite dilution, Henry's law constants at each temperature were obtained by taking the limit as the mole fraction of CO₂ approaches zero.

4. Results and discussion

Experimental solubility isotherms of five ionic liquids including [S₂₂₂][Tf₂N], [deme][Tf₂N], [pmim][Tf₂N], [amim][Tf₂N], and [4mbp][BF₄] were measured at 313.15, 323.15 and 333.15 K at different pressures up to 20 bar using an Intelligent Gravimetric Analyzer (IGA-003) manufactured by Hiden Isochema. A graphical representation of our solubility data in Figure 1 is presented, where solubility data is shown as a function of pressure at different temperatures for all of the studied ionic liquids. Solubilities of CO₂ in the ionic liquids are dramatically affected by temperature and pressure. The solubility decreases as temperature increases and pressure decreases.

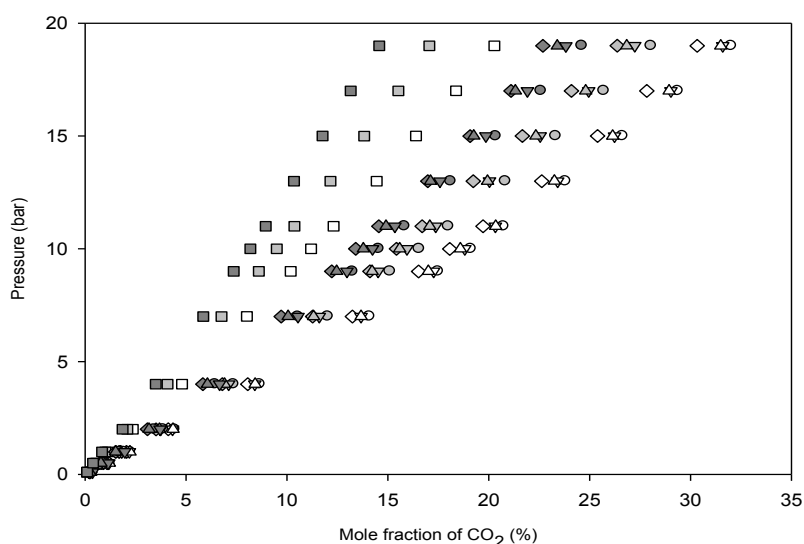


Figure 1: Comparison of measured isothermal solubility data of CO₂ in different ionic liquids: ■, [4mbp][BF₄]; ◆, [S₂₂₂][Tf₂N]; ▲, [amim][Tf₂N]; ▼, [pmim][Tf₂N]; ●, [deme][Tf₂N]; white, at 313.15 K; gray, at 323.15 K; dark gray, at 333.15 K

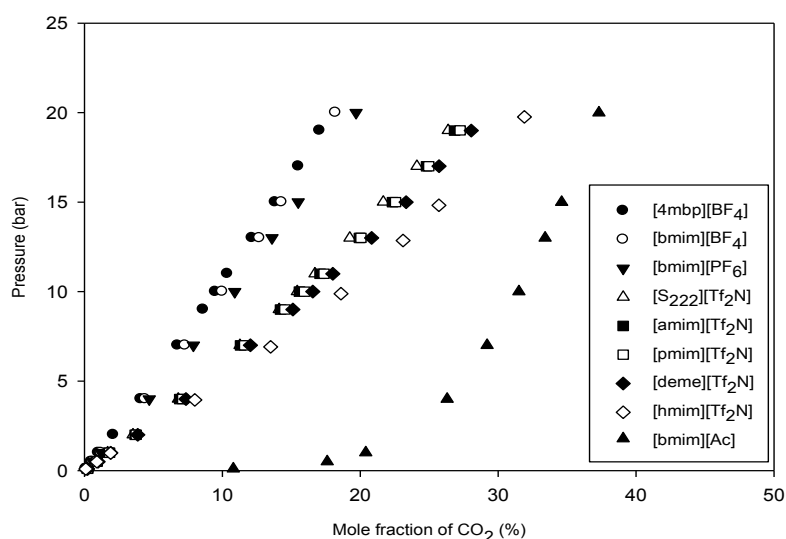


Figure 2: Comparison between the solubility of CO₂ in the studied ionic liquids and the published ones in the literature at 323.15 K: ●, [4mbp][BF₄] (This work); ○, [bmim][BF₄] (Shiflett and Yokozeki, 2005); ▼, [bmim][PF₆] (Shiflett and Yokozeki, 2005); △, [S₂₂₂][Tf₂N] (This work); ■, [amim][Tf₂N] (This work); □, [pmim][Tf₂N] (This work); ◆, [deme][Tf₂N] (This work); ◇, [hmim][Tf₂N] (Shiflett and Yokozeki, 2007); ▲, [bmim][Ac] (Shiflett et al., 2008)

As shown in Figure 2, the solubility of CO₂ in the investigated ionic liquids was compared to those published by Shiflett and co-workers (Shiflett and Yokozeki, 2005, Shiflett and Yokozeki, 2007, Shiflett et al., 2008). Considering the studied ionic liquids based on the [Tf₂N⁻] anion to understand the effect of cation, the ionic liquid with ammonium-based cation, [deme][Tf₂N], apparently shows the highest CO₂ absorption. Meanwhile, [4mbp][BF₄] had the lowest CO₂ solubility among the ionic liquids studied due to the effect of the anion [BF₄⁻] anion which has less fluorination. Nevertheless, the solubility in [4mbp][BF₄] is comparable to that in [bmim][BF₄] (Shiflett and Yokozeki, 2005), and less than that in [bmim][PF₆] (Shiflett and Yokozeki, 2005), an ionic liquid with higher fluorination level. Between the two ionic liquids with C₃ alkyl chain ([pmim][Tf₂N] and [amim][Tf₂N]), the cation structure of [amim][Tf₂N] contains a double bond on the C₃ alkyl position, whereas [pmim][Tf₂N] contains only a single bond on the alkyl chain [pmim][Tf₂N]. The solubility results indicate that [pmim][Tf₂N] exhibits higher CO₂ absorption than [amim][Tf₂N]. According to Sumon and Henni (2011), Henry's law constant of CO₂ in ionic liquids decreased as the polarity of ionic liquids decreased. An equivalent meaning of the statement implies that the solubility of CO₂ in ionic liquids is enhanced by a decrease in their polarity. Therefore, the presence of a double bond on the alkyl chain of the cation of [amim][Tf₂N] which leads to higher polarity of the ionic liquid apparently lowers the solubility of CO₂. The absorption of CO₂ in the ionic liquids is prone to decrease due to the effect of the structural variation of the cations and anions in this sequence: [deme][Tf₂N] > [pmim][Tf₂N] > [amim][Tf₂N] > [S₂₂₂][Tf₂N] > [4mbp][BF₄]. The four ionic liquids ([deme][Tf₂N], [pmim][Tf₂N], [amim][Tf₂N] and [S₂₂₂][Tf₂N]) are deemed potential solvents for CO₂ capture because of high CO₂ solubility with physical absorption. These salts are competitive to the physically CO₂-absorbing ionic liquids presenting high CO₂ solubility, [hmim][Tf₂N] (Shiflett and Yokozeki, 2007). Despite the high physical CO₂ absorption of the four promising ionic liquids, it is apparent that the solubility of CO₂ is much less than that in [bmim][Ac] (Shiflett et al., 2008), owing to the presence of the intermolecular chemical complex formations during CO₂ absorption. However, such chemical complexes require intensive heat in order to regenerate the solvents. A graphical display of Henry's law constants for CO₂ in [S₂₂₂][Tf₂N], [deme][Tf₂N], [pmim][Tf₂N], [amim][Tf₂N], and [4mbp][BF₄] at three temperatures of 313.15, 323.15, and 333.15 K is presented in Figure 3. The values of the Henry's law constants are reported in Table 2. . In comparison to the ionic liquids containing the [Tf₂N⁻] anion, trivial differences in the Henry's law constants for CO₂ in these ionic liquids emphasize that the cations have insignificant influence on the CO₂ solubility. The four ionic liquids with [Tf₂N⁻] anion, [S₂₂₂][Tf₂N], [deme][Tf₂N], [pmim][Tf₂N], and [amim][Tf₂N], exhibit a relatively high affinity for CO₂ when compared to [4mbp][BF₄].

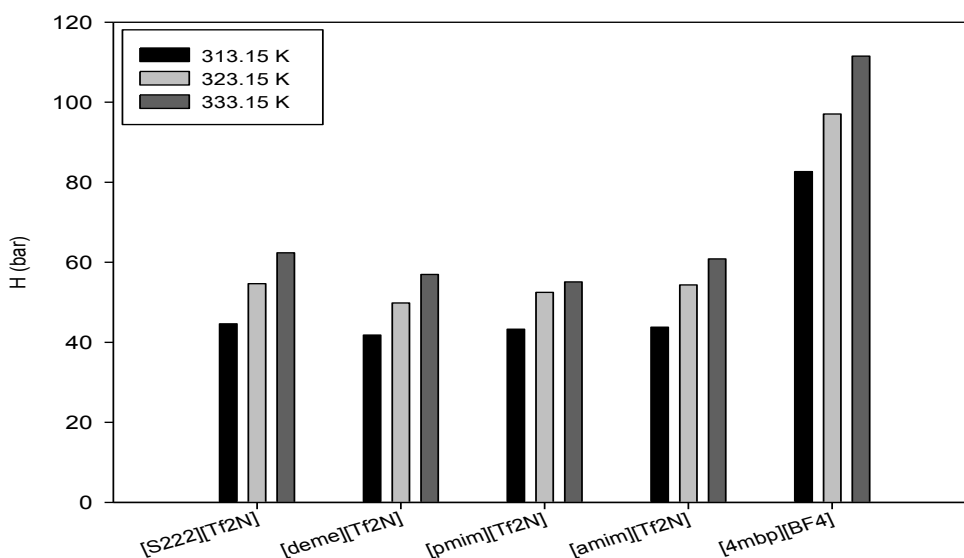


Figure 3: Henry's law constants for CO₂ in [S₂₂₂][Tf₂N], [deme][Tf₂N], [pmim][Tf₂N], [amim][Tf₂N] and [4mbp][BF₄] at 313.15, 323.15 and 333.15 K

Table 2: Henry's law constants for CO₂ in the studied ionic liquids

Ionic liquids	H _{2,1} (bar)		
	313.15 K	323.15 K	333.15 K
[S ₂₂₂][Tf ₂ N]	44.6	54.7	62.4
[deme][Tf ₂ N]	41.8	49.8	56.9
[pmim][Tf ₂ N]	43.3	52.5	55.1
[amim][Tf ₂ N]	43.8	54.3	60.8
[4mbp][BF ₄]	82.7	97.1	111.5

5. Conclusion

Measurements of CO₂ solubility in five ionic liquids, triethylsulfonium bis(trifluoromethylsulfonyl)imide ([S₂₂₂][Tf₂N]), diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ([deme][Tf₂N]), 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([pmim][Tf₂N]), 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([amim][Tf₂N]), and 1-butyl-4-methylpyridinium tetrafluoroborate ([4mbp][BF₄]) were reported at three temperatures (313.15, 323.15 and 333.15 K) and at pressures up to 20 bar using a gravimetric microbalance. For all ionic liquids studied, the solubility decreased as temperature increased and pressure decreased. The trend of the investigated ionic liquids in terms of solubility of CO₂ was reported as: [deme][Tf₂N] > [pmim][Tf₂N] > [amim][Tf₂N] > [S₂₂₂][Tf₂N] > [4mbp][BF₄]. The four ionic liquids ([deme][Tf₂N], [pmim][Tf₂N], [amim][Tf₂N] and [S₂₂₂][Tf₂N]) can be considered promising solvent alternatives for CO₂ capture because of their high physical capacity in absorbing CO₂.

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