



# High pressure phase behaviour of carbon dioxide and two ionic liquids based on a benzyl functionalized cation

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## ABSTRACT

The high pressure phase behaviour of a CO<sub>2</sub> and 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BzMeIM][NTf<sub>2</sub>], binary system was experimentally measured at high pressure up to about 13.5 MPa and at a temperatures range of 293.2–323.2 K. The solubilities were determined by measuring the bubble point pressure of the binary mixture comprising CO<sub>2</sub> and an ionic liquid using a phase equilibrium apparatus including a high pressure variable-view cell. The effect of a benzyl functional group in different cations, imidazolium and pyridinium, on the high pressure phase behaviour of the CO<sub>2</sub> and 1-benzylpyridinium bis(trifluoromethylsulfonyl)imide, [BzPY][NTf<sub>2</sub>], binary system was also investigated within similar temperature and CO<sub>2</sub> mole fractions ranges. The experimental data correlated well with the Peng-Robinson equation of state. In general, higher CO<sub>2</sub> solubilities were obtained in [BzPY][NTf<sub>2</sub>] than those in [BzMeIM][NTf<sub>2</sub>] at similar temperature and pressure. This may be attributed to the difference in aromaticity in pyridinium and imidazolium cations.

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## 1. Introduction

Several processes to separate carbon dioxide, which is considered a primary cause, among many greenhouse gases, of global warming, have been proposed. The most widely applied process is based on absorption in the presence of aqueous solutions of amines [1]. However, there is a great deal of room to mitigate the drawbacks of using amine solutions in absorption, including loss of the volatile solvent and serious corrosion and high energy cost for solvent recovery [2]. Ionic liquids have been applied as an amine solvent replacement because they have desired physical properties [3], such as, negligible vapour pressure, non-flammability, and tunable ability by varying anions and/or cations depending on the field employed.

Anthony et al. [4] reported the effects of anion on CO<sub>2</sub> solubility in ionic liquids incorporating bis(trifluoromethylsulfonyl)imide, [NTf<sub>2</sub>], and reported that the anion based ionic liquids had much higher CO<sub>2</sub> solubility than any other anion based ionic liquids. For example, the Henry constants of CO<sub>2</sub> in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM][NTf<sub>2</sub>], in [BMIM][PF<sub>6</sub>], and [BMIM][BF<sub>4</sub>], were (3.3, 5.34, and 5.9) MPa, respectively. This may be due to the nonspecific van der Waals interactions because [NTf<sub>2</sub>] is much bigger than [BF<sub>4</sub>] and

[PF<sub>6</sub>]. These experimental results were theoretically supported by applying a conductor-like screening model for realistic solvation (COSMO-RS) model [5].

The linear relationship between the alkyl chain length on the imidazolium cation and CO<sub>2</sub> solubility has been revealed by several researchers [6–8]. While CO<sub>2</sub> solubilities in imidazolium cation based ionic liquids were nearly the same at lower pressures, in a high-pressure range, the CO<sub>2</sub> solubility increased according to the length of the 1-alkyl chain from ethyl to octyl in the cation of 1-alkyl-3-methylimidazolium based ionic liquid. This behaviour was explained by both entropic and enthalpic effects because the partial molar enthalpy was slightly higher than the product of the temperature and the partial molar entropy [8]. In addition to the bubble point pressures, the cloud point pressures were also reported depending on the CO<sub>2</sub> mole fraction as well as the chemical structure of the ionic liquid used in a CO<sub>2</sub> and ionic liquid binary system [7].

While imidazolium based ionic liquids have been the most widely studied ionic liquids with respect to physical absorption of CO<sub>2</sub>, pyridinium based ionic liquids are less costly and more easily biodegradable with similar performance [9]. As in the case of imidazolium based ionic liquids, as longer alkyl group chains in the pyridinium based cation are incorporated, the CO<sub>2</sub> solubility in an ionic liquid becomes accordingly higher [10], when [NTf<sub>2</sub>] is used as an anion counterpart. For instance, the CO<sub>2</sub> solubility increased from 0.200 to 0.233 when the alkyl chain length in the pyridinium cation of a butylpyridinium cation based ionic liquid

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was increased to a dodecylpyridinium based ionic liquid. Aki et al. [11] explained this dependence of the alkyl chain length on the CO<sub>2</sub> solubility by an entropic rather than an enthalpic effect, due to the increase of the compounds sizes with an increase of the alkyl chain length leading to a greater free volume.

In addition to the systematic study of the effect of the alkyl chain length in cations on the CO<sub>2</sub> solubility, the influence of functional groups on ionic liquids was also investigated. The functional groups that have been studied include amines [12], amino acids [13], and alcohol [14]. The reason for the huge increase in CO<sub>2</sub> solubility in the presence of an amine-functionalized imidazolium cation based ionic liquid was the formation of carbamate between one mole of CO<sub>2</sub> and two moles of ionic liquids [12]. An order of magnitude increase in CO<sub>2</sub> solubility in the presence of the above functional groups is attributed to the formation of chemical bonds between CO<sub>2</sub> and functionalized ionic liquids. To the authors' best knowledge the effect of the presence of a benzyl functional group on a cation based ionic liquid on the CO<sub>2</sub> solubility has not been reported to date.

As a continuation of our efforts [15–17] to understand the effect of substituents in ionic liquids on CO<sub>2</sub> solubility, we chose [NTf<sub>2</sub>] as an anion, while benzyl group functionalized imidazolium and pyridinium cations, namely, 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BzMeIM][NTf<sub>2</sub>], and 1-benzylpyridinium bis(trifluoromethylsulfonyl)imide, [BzPY][NTf<sub>2</sub>], were also selected. We determined the CO<sub>2</sub> solubility in both [BzMeIM][NTf<sub>2</sub>] and [BzPY][NTf<sub>2</sub>] ionic liquids using a high pressure variable-volume view cell. The solubility was measured by determining the bubble point pressure for two binary systems by varying the temperature from 293.2 K to 323.2 K with a known composition of each compound. The obtained experimental results were correlated with the Peng-Robinson equation of state (PR-EoS).

## 2. Experimental

### 2.1. Chemicals

[BzMeIM][NTf<sub>2</sub>] and [BzPY][NTf<sub>2</sub>] were bought from C-tri Inc. (Suwon, Korea). Both [BzMeIM][NTf<sub>2</sub>] and [BzPY][NTf<sub>2</sub>] are >0.98 mass fraction purity, as can be seen in Table 1, and the residual chloride content is below 100 ppm. The water content of [BzMeIM][NTf<sub>2</sub>] and [BzPY][NTf<sub>2</sub>], measured using Karl Fischer moisture analyzer (Model V20, Mettler Toledo Inc.), was 200 ppm (1 ppm = 10<sup>-6</sup> mass fraction). The SFC grade carbon dioxide (99.99%) was supplied by Sebotech Inc. (Daejeon, Korea). All the chemicals were used as received without further purification. The structure of the ILs used in this study was confirmed by a nuclear magnetic resonance (NMR) spectrometer (Figs. S1-1, S1-2, S2-1, and S2-2 in Supporting Information).

### 2.2. Experimental apparatus and method

The details of the experiment apparatus and method applied to determine the bubble point and cloud point pressures have already

been described [15]. In brief, the apparatus comprises a variable volume view cell with a 43.8 cm<sup>3</sup> volume, hand pump, syringe pump (Teledyne Isco Inc., model 260D), and pressure indicator (Heise model 901B, 0–5000 psi range, accuracy: ±0.07%). The temperature of the cell was controlled using a water bath (Jeio Tech. Inc., model RW-0525G, accuracy: ±0.1 K). A fixed amount (~15 g) of ionic liquid was initially loaded into the view cell using a syringe. To remove any impurities from the liquid phase the cell was vacuumed for a couple of hours at room temperature. A known amount of CO<sub>2</sub> was then loaded into the view cell using a syringe pump operated at constant temperature and pressure. The mass of CO<sub>2</sub> loaded into the view cell was determined on the basis of the difference in the volume of the syringe pump before and after CO<sub>2</sub> was introduced at constant temperature and pressure as well as density, which was obtained from the NIST website [18].

The pressure was varied until a phase change was visually observed. At a fixed temperature and composition, the bubble point pressure was defined as the pressure at which the first bubbles were observed. As Shin and co-workers used [7], the cloud point was obtained when the solution becomes cloudy due to the phase transition from a single to a liquid-liquid phases. Every measurement was carried out at least five times for each condition to ensure consistency in the experimental results.

## 3. Modelling

Because Ionic Liquids have negligible vapour pressure we assume that there is no ionic liquid in the vapour phase. The fugacity of CO<sub>2</sub> (1) in the vapour phase and that in the liquid phase are equal at equilibrium, as shown below:

$$f_1^v = \hat{f}_1^l \quad (1)$$

where  $f_1^v$  is the fugacity of CO<sub>2</sub> in the vapour phase and  $\hat{f}_1^l$  is that in the liquid phase. PR-EoS has been applied to correlate the experimental data and is given in Eq. (2).

$$P = \frac{RT}{v - b_m} - \frac{a_m}{v(v + b_m) + b_m(v - b_m)} \quad (2)$$

where  $a_m$  and  $b_m$  are the attractive and co-volume parameters, respectively, of the mixture. The mixture parameters,  $a_m$  and  $b_m$ , are estimated using the mixing rules, as shown below:

$$a_m = \sum_{i=1} \sum_{j=1} x_i x_j a_{ij} \quad (3)$$

$$b_m = \sum_{i=1} \sum_{j=1} x_i x_j b_{ij} \quad (4)$$

where

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (5)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (6)$$

where  $k_{ij}$  and  $l_{ij}$  are the binary interaction parameters.

**Table 1**  
Source of the chemicals used, and purity as stated by the suppliers.

Chemical name <sup>a</sup>	Source	Water content/10 <sup>-6b</sup>	Initial mass fraction purity	Purification method	Final weight fraction purity	Analysis method
[BzMeIM][NTf <sub>2</sub> ]	C-tri Inc.	<200	>0.98	None	–	–
[BzPY][NTf <sub>2</sub> ]	C-tri Inc.	<200	>0.98	None	–	–
CO <sub>2</sub>	Sebotech Inc.	N/A <sup>c</sup>	0.9999 <sup>d</sup>	None	–	–

<sup>a</sup> [BzMeIM][NTf<sub>2</sub>]: 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; [BzPY][NTf<sub>2</sub>]: 1-benzylpyridinium bis(trifluoromethylsulfonyl)imide.

<sup>b</sup> 1 ppm = 10<sup>-6</sup> mass fraction.

<sup>c</sup> N/A: not applicable.

<sup>d</sup> Mole fraction purity.

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