

## **REMOVAL OF CO<sub>2</sub> FROM NATURAL GAS USING IONIC LIQUIDS**

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## 1. ABSTRACT

Natural gas is used mainly as a fuel and also as a raw material for petrochemical industry. It is regarded as an environmentally friendly clean fuel compared to other fossil fuel. However, the presence of carbon dioxide, CO<sub>2</sub> gas lowers the fuel value of natural gas and therefore need to be removed. The most commonly used technique to remove CO<sub>2</sub> is by chemically absorbing CO<sub>2</sub> with aqueous alkanolamines. However, there are some disadvantages of the current process in such that the aqueous solution will undergo degradation, the enthalpy of reaction for the chemical absorption of CO<sub>2</sub> is high in addition to corrosion and fouling problems of the process. Currently, ionic liquids are under intense investigation as a potential replacement for solvents in reaction and separation processes. In the separation of CO<sub>2</sub> from natural gas, ionic liquids are being proposed as potential solvents to absorb CO<sub>2</sub>. To date, several ionic liquids, mostly imidazolium-based ionic liquids were successfully applied in absorbing CO<sub>2</sub> under experimental conditions. In this work, lower cost of ionic liquids from a different class of cation namely pyridinium based, were synthesized and characterized. The low pressure solubility of CO<sub>2</sub> in these ionic liquids was determined using a Magnetic Suspension Balance (MSB) equipment at temperatures of 298.15K, 313.15K and 333.15K and pressure range of (0.99 – 12.53) bar. The effect of using different cation's alkyl chain length was also presented. The CO<sub>2</sub> solubility results were compared with published data obtained from literature using imidazolium based ionic liquids. Additionally, the solubility of methane, CH<sub>4</sub> and nitrogen, N<sub>2</sub> in these ionic liquids at 298.15K and pressure of (1.00 – 10.03) bar were also measured and compared with that of CO<sub>2</sub>. Results show that the pyridinium based ionic liquids have potential to be used as solvents to remove CO<sub>2</sub> from natural gas.

## TABLE OF CONTENTS

1. Abstract
2. Introduction
3. Experimental
4. Results and discussions
5. Conclusions
6. References
7. List of figures
8. List of tables

## 2. INTRODUCTION

Natural gas which is used mainly as a fuel is regarded as an environmentally friendly clean fuel [1]. It comprises mainly of methane with varying amount of other hydrocarbon such as ethane, propane and butane. The raw natural gas obtained from the most gases field also contains nitrogen, carbon dioxide and hydrogen sulphide. The composition varies widely depending on the location and geological formation of the reservoir. Removal of acid gases components, such as carbon dioxide (CO<sub>2</sub>) and hydrogen sulphide (H<sub>2</sub>S), from the raw natural gas stream is a very important process. This is due to the fact that CO<sub>2</sub> is a non-combustible gas and its presence in the natural gas stream lowers the fuel value of the natural gas. On the other hand, H<sub>2</sub>S burns but is considered highly toxic as its' combustion produces noxious and corrosive sulphur oxides [2]. High capacity absorbents coupled with high efficient contactors are now required to be used in the conventional absorption process in order to remove CO<sub>2</sub> from the natural gas. Previously, the most widely used technology is based on absorption using aqueous alkanolamines as the solvent. Typical alkanolamines used are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), and 2-amino-2-methyl-1-propanol (AMP) or any combination of alkanolamine solutions. Aqueous MEA solution has been the most selected absorbents used industrially due to its rapid reaction rate, low cost of solvent, thermal stability and low solubility of hydrocarbons and high alkalinity [3]. However, usage of MEA has its drawback such as the solvent is subjected to degradation, high enthalpy of reaction and corrosion problems. Conversely, MDEA which is a tertiary amine, although is better than the primary or secondary amine such as MEA and DEA, in the sense that it has higher CO<sub>2</sub> loading capacity per mole of absorbent, less regeneration of energy and high resistance to thermal degradation [3], but the reaction rate of the tertiary alkanolamines are comparably low than that of primary or secondary amines.

The purging of the natural gas stream through the alkanolamines absorbent to remove acid gases usually creates problems. For a start, although the exiting gas stream is acid gas free, it has been thoroughly saturated with water vapour which has to be removed thus resulting in energy intensive condensation step. At the same time, some of the alkanolamines may also be taken up into the gas stream. This loss has an impact to the economics of the absorption process. Besides that, the extrusion of CO<sub>2</sub> from the loaded or spent scrubbing fluid may require the heating of the solution, which in turn involves heating the solvating water along with the reagent and thus gives unwanted energy cost [2]. In view of these problems, researchers are looking for better solvents for the capture of various acid gases and ionic liquids are considered as one of the promising alternative.

Ionic liquids are liquids that are comprised entirely of ions [4]. They are considered as new solvents which possesses a number of unique properties such as high chemical stability, wide liquid temperature range (approximate 300K), good solvents for polar, non-polar, organic and inorganic compounds, and non detectable vapour pressure thus non-flammable. There is unlimited possible combination of cations and anions which could be paired to form an ionic liquid. Depending on the type of cation and anion used, the ionic liquids could be designed to meet specific application. Nowadays, ionic liquids have found numerous applications such as in gas separations, liquid separations, catalytic reactions, electrolyte/fuel cells, pharmaceutical and many others.

In gas separations, a number of publications have shown the potential of ionic liquids in absorbing CO<sub>2</sub>. However, in-depth understanding on the mechanism of the CO<sub>2</sub> gas solubility in ionic liquids is important prior to its utilization for CO<sub>2</sub> removal from the natural gas mixture. The phase behaviour and the solubility of some gases in several ionic liquids have been studied by few authors using mainly imidazolium based ionic liquids with different class of anions to investigate the relationship of CO<sub>2</sub> absorbing capability and the nature or type of the ionic liquids [5-9]. Results showed that ionic liquids with fluorinated anion were able to absorb more CO<sub>2</sub> in comparison with other anions. In addition, the CO<sub>2</sub> solubility increases with the alkyl chain of the cation. In this work, lower cost ionic liquids from a different class of cation namely pyridinium based, were synthesized and characterized. Their potential of absorbing CO<sub>2</sub> was then tested using a gravimetric method employed on a Magnetic Suspension Balance (MSB) equipment. The impact from using different cation's alkyl chain length were also studied. The results were

compared with similar results obtained from literature using imidazolium-based ionic liquids. Additionally, the solubility of methane (CH<sub>4</sub>) and nitrogen (N<sub>2</sub>) in these ionic liquids were also measured and compared with that of CO<sub>2</sub>.

### 3. EXPERIMENTAL

#### 3.1 Materials

Chemicals of analytical grade were used for the synthesis of the ionic liquids. The CAS number, source, and grades of the chemical used are as follows: pyridine (110-86-1, Fisher Scientific, 99.99%), ethyl acetate (anhydrous, 141-78-6, Fisher Scientific, 99.98%), 1-bromobutane (109-65-9, Merck, ≥98%), 1-bromododecane (143-15-7, Acros Organic, 98%) and lithium bis(trifluoromethylsulfonyl)imide, LiTf<sub>2</sub>N (90076-65-6, Acros Organic, 99%). All chemicals were used without further purification. CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> used in the solubility experiment supplied by Malaysia Oxygen Berhad with purity of >99.99%, >99.5%, >99.999%, respectively.

#### 3.2 Synthesis

The ionic liquids used in the present research were synthesized according to the established methods [10-12]. [C<sub>*n*</sub>py][Tf<sub>2</sub>N] where *n* = 4 or 12 were prepared through anion exchange reaction between [C<sub>*n*</sub>py][Br] and LiTf<sub>2</sub>N. For the preparation of [C<sub>4</sub>py][Br], pyridine (0.25 mol) was refluxed with 1-bromobutane (0.29 mol) in 50 mL ethyl acetate at 50°C for 72 hours under nitrogen atmosphere. The product was purified using recrystallization method with ethyl acetate as the solvent and dried under reduced pressure at 70°C for a few hours and finally in vacuum oven for 24 hours to remove the solvent completely. Similar method was used to prepare [C<sub>12</sub>py][Br] except that the temperature was raised to 70°C for 240 hours for the completion of the reaction. For the preparation of [C<sub>*n*</sub>py][Tf<sub>2</sub>N], equimolar [C<sub>*n*</sub>py][Br] and LiTf<sub>2</sub>N were mixed in deionised water and stirred at room temperature for 24 hours. The product was separated from the aqueous phase and washed several times with deionised water until the washed water passed silver nitrate test indicating the absence of bromide ion. The product was dried under reduced pressure at 70°C for a few hours and finally in vacuum oven for 3 days to remove the water solvent. The structure of [C<sub>*n*</sub>py][Tf<sub>2</sub>N] is shown in figure 1.

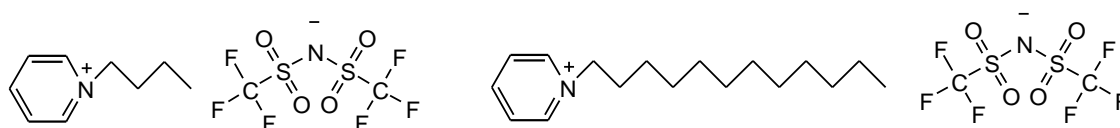


Figure 1: Structure of [C<sub>4</sub>py][Tf<sub>2</sub>N] (left) and [C<sub>12</sub>py][Tf<sub>2</sub>N] (right).

#### 3.3 Purity measurement and characterization

The purity of the ionic liquids was verified using Nuclear Magnetic Resonance (NMR) spectroscopy. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at room temperature on JEOL JNM-ECA400 or Bruker DRX300 spectrometer. The <sup>1</sup>H and <sup>13</sup>C chemical shifts ( $\delta$ ) are reported in parts per million (ppm) reference with TMS as an internal standard. Multiplicities are abbreviated as *s* = singlet, *d* = doublet, *t* = triplet, and *m* = multiplet. Microanalysis to determine the individual percentage of elements in the products was done using CHNS-932 (LECO Instruments) elemental analyzer. The water content of the ionic liquids was determined using coulometric Karl Fischer autotitrator, Mettler Toledo DL39 with CombiCoulomat fritless Karl Fischer reagent (Merck). The bromide content was determined by ion chromatography Metrohm Model 761 Compact IC. The data was analysed using Metrodata IC Net 2.3 software.

The densities of the ionic liquids were measured at temperatures from 293.15 to 353.15K using a rotational automated Anton Paar Stabinger Viscometer SVM3000 with the measurement's reproducibility

of  $\pm 5 \times 10^{-4} \text{ g.cm}^{-3}$  and temperature accuracy of  $\pm 0.02^\circ\text{C}$ . The decomposition temperatures of the ionic liquids at heating rates of  $10^\circ\text{Cmin}^{-1}$  and  $20^\circ\text{Cmin}^{-1}$  were determined using thermogravimetric analyzer, TGA, Perkin Elmer Pyris V-3.81 under nitrogen atmosphere.

### 3.4 CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> absorption measurements

The solubility of the gases in the ionic liquids were measured using gravimetric technique. A magnetic suspension balance (MSB) from Rubotherm Präzisionsmesstechnik GmbH was used in this study. The balance with mass precision of  $\pm 20\mu\text{g}$ , is magnetically coupled to the sorption chamber by means of an electromagnet and a suspension magnet and thus keeping the balance at ambient conditions during the absorption measurements. The balance records the change in weight of the sample upon absorption of the gas. In a typical experiment, about 1g of ionic liquid sample is placed in a sample basket and loaded in the absorption chamber. The sample is then evacuated at temperature of  $100^\circ\text{C}$  at  $10^{-3}$  mbar (Pfeiffer model DUO5) to remove any water, solvents or dissolved gases for at least 48 hours or until the weight remains constant. The temperature of the absorption chamber is controlled by an oil circulator (Julabo model F25-ME) with an accuracy of  $\pm 0.1^\circ\text{C}$ . The chamber is then pressurized with CO<sub>2</sub> which was previously dried using molecular sieve at constant temperature and the weight is monitored as the gas dissolves into the sample. Once the weight reaches constant value, it is maintained at that condition for at least 2 hours to ensure complete equilibration before the pressure of the system is increased to other value. The desorption isotherm is also measured by incrementally evacuating the gas from the system. Similar method is employed to measure the absorption of N<sub>2</sub> and CH<sub>4</sub>. The mass of the gas dissolved in the ionic liquid,  $w_g$ , is calculated using the following equation after considering the gas buoyancy [13]:

$$w_g = w_1(P, T) - w_0(0, T) + \rho_g(P, T) \cdot (V_{SC+S}) \quad (1)$$

where  $w_1$  and  $w_0$  are the corrected weights of the balance at pressure,  $P$  and temperature,  $T$  and zero pressure, respectively.  $\rho$  is the gas density, ( $\text{g.cm}^{-3}$ ) and  $V_{SC}$  and  $V_S$  ( $\text{cm}^3$ ) are the volumes of the sample container and sample, respectively. For ionic liquids, it was assumed that the change in volume due to expansion is negligible [5]. The densities of the gases were calculated using the following equations of state: equation of state developed by Span and Wagner [14] for CO<sub>2</sub>, Setzmann and Wagner, 1991[15] for CH<sub>4</sub> and Span et al., 2000 [16] for N<sub>2</sub>.

## 4. RESULTS AND DISCUSSIONS

All the details and results for purity and characterization measurements have been published previously [12]. However some of the results are published again here for reference purposes.

[C<sub>4</sub>py][Tf<sub>2</sub>N]; <sup>1</sup>H NMR (400 MHz, MeOD):  $\delta$  8.8279 [d, 2H (py)], 8.4724 [t, 1H (py)], 7.9769 [t, 2H (py)], 4.5226 [t, 2H, N-CH<sub>2</sub>], 1.9421 – 1.8664 [m, 2H, CH<sub>2</sub>], 1.3549 – 1.2609 [m, 2H, CH<sub>2</sub>], 0.8755 [t, 3H, CH<sub>3</sub>], <sup>13</sup>C NMR (100 MHz, MeOD):  $\delta$  146.6750, 145.6056, 129.3686, 120.9827, 62.8797, 34.1199, 20.1253, 13.5362.

Analysis % found (% calculated), C, 31.6 (31.7); H, 3.3 (3.4), N, 6.6 (6.7), S, 15.6 (15.4); water 172 ppm, bromide 85 ppm; thermal decomposition temperature, T<sub>d</sub> ( $10^\circ\text{Cmin}^{-1}$ ) 697K, ( $20^\circ\text{Cmin}^{-1}$ ) 719K.

[C<sub>12</sub>py][Tf<sub>2</sub>N]: <sup>1</sup>H NMR (300 MHz, MeOD):  $\delta$  8.986 [d, 2H (py)], 8.586 [t, 1H (py)], 8.103 [t, 2H (py)], 4.616 [t, 2H, N-CH<sub>2</sub>], 2.014 – 1.279 [m, 20H, (CH<sub>2</sub>)<sub>10</sub>], 0.887 [t, 3H, CH<sub>3</sub>], <sup>13</sup>C NMR (75 MHz, MeOD):  $\delta$  146.843, 145.886, 129.500, 121.146, 63.157, 33.041, 32.449, 30.696, 30.684, 30.574, 30.437, 30.052, 27.140, 23.707, 14.412.

Analysis % found (% calculated), C, 43.0 (43.2); H, 5.8 (5.7), N, 5.2 (5.3), S, 11.9 (12.1); water 253 ppm, bromide 50 ppm; thermal decomposition temperature, T<sub>d</sub> ( $10^\circ\text{Cmin}^{-1}$ ) 673K, ( $20^\circ\text{Cmin}^{-1}$ ) 681K.

T/K	$\rho$ (g.cm <sup>-3</sup> )	
	[C <sub>4</sub> py][Tf <sub>2</sub> N]	[C <sub>12</sub> py][Tf <sub>2</sub> N]
293.15	1.4525	1.2531
298.15	1.4476	1.2488
303.15	1.4429	1.2446
308.15	1.4383	1.2405
313.15	1.4336	1.2364
318.15	1.4290	1.2323
323.15	1.4243	1.2282
328.15	1.4197	1.2241
333.15	1.4151	1.2201
338.15	1.4105	1.2160
343.15	1.4060	1.2120
348.15	1.4015	1.2080
353.15	1.3970	1.2040

Table 1: Experimental density ( $\rho$ ) values of [C<sub>n</sub>py][Tf<sub>2</sub>N] at temperatures (293.15 – 353.15)K.

In the present work, the low pressure solubility of carbon dioxide, CO<sub>2</sub> in two pyridinium based ionic liquids; 1-butylpyridinium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>py][Tf<sub>2</sub>N] and 1-dodecylpyridinium bis(trifluoromethylsulfonyl)imide [C<sub>12</sub>py][Tf<sub>2</sub>N] were measured at temperatures 298.15K, 313.15K and 333.15K and in the pressure range of (1.00 – 12.53) bar. In addition, the solubility of CH<sub>4</sub> and N<sub>2</sub> were also measured at 298.15K and in the pressure range of (1.00 – 10.03) bar. The results are presented in figures 2 – 7. The Henry's law constants,  $K_H$  for the solubility of the gases in the ionic liquids are also estimated. The Henry's law constant  $K_H$  is defined as [17]:

$$K_H(p, T, x_2) = \lim_{x_2 \rightarrow 0} \frac{f_2(p, T, x_2)}{x_2} \quad (2)$$

where  $f_2$  is the fugacity of the gas dissolved in the liquid phase. Henry's law constant is strongly dependent on temperature, but weakly dependent on pressure. Since ionic liquids have negligible vapour pressure, the fugacity of the gas in the gas-ionic liquid system is assumed to be equal to the pure gas. The fugacity of the pure gas is expressed as:

$$f_2(p, T) = p_{eq} \phi_2(p_{eq}, T_{eq}) \quad (3)$$

in which the  $\phi_2$  fugacity coefficient and is calculated using SRK equation of state. Combining equations (2) and (3) gives:

$$K_H(p, T, x_2) \cong \frac{\phi_2(p_{eq}, T_{eq}) p_{eq}}{x_2} \quad (4)$$

The present experimental values of the low pressure solubility of CO<sub>2</sub> in the pyridinium based ionic liquids are presented in figures 2-4 for the pressure and temperature range studied. Figure 2 shows the absorption and desorption of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] and [C<sub>12</sub>py][Tf<sub>2</sub>N] at 298.15K. From the figure, it is shown that the solubility of CO<sub>2</sub> in the ionic liquids increases with CO<sub>2</sub> pressure for both ionic liquids. In addition, the absorption and desorption points are almost indistinguishable for both ionic liquids as shown in the figure. Figures 3 and 4 show the effect of different temperature on the absorption of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] and [C<sub>12</sub>py][Tf<sub>2</sub>N] at 298.15K, 313.15K and 333.15K and in the pressure range of (0.99 – 8.03) bar. Increasing the absorption temperature will decrease the amount of CO<sub>2</sub> absorbed in the ionic liquids. Similar observations for both effects of pressure and temperature are seen in CO<sub>2</sub> absorption in

other ionic liquids as available in literature [5-9]. Figure 2 shows that the solubility of CO<sub>2</sub> is higher in [C<sub>12</sub>py][Tf<sub>2</sub>N] than that of [C<sub>4</sub>py][Tf<sub>2</sub>N] for the range of pressure and temperature studied. However the increment is not that significant, for example from 0.285 mol fraction CO<sub>2</sub> for [C<sub>4</sub>py][Tf<sub>2</sub>N] to 0.333 mol fraction CO<sub>2</sub> for [C<sub>12</sub>py][Tf<sub>2</sub>N] at the 298.15K and 12.53 bar which is about 17% of increment. Based on table 1, it is seen that the density of [C<sub>4</sub>py][Tf<sub>2</sub>N] is greater than that of [C<sub>12</sub>py][Tf<sub>2</sub>N] for all the measured temperatures. Increasing the alkyl chain of the ionic liquid will decrease the density of the ionic liquid and subsequently increasing the free volume in the ionic liquid. More CO<sub>2</sub> can dissolve if the ionic liquid has more free volume [18].

Figure 5 shows the comparison of the measured CO<sub>2</sub> solubility at 298.15K in [C<sub>4</sub>py][Tf<sub>2</sub>N] and [C<sub>12</sub>py][Tf<sub>2</sub>N] with 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>2</sub>mim][Tf<sub>2</sub>N] [9], 1-methyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>4</sub>mim][Tf<sub>2</sub>N] [8] and 1-methyl-3-hexylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>6</sub>mim][Tf<sub>2</sub>N] [19]. It seems that the absorption capacity is not very much affected by these two different types of cation. The absorption points of CO<sub>2</sub> in [C<sub>4</sub>mim][Tf<sub>2</sub>N] and [C<sub>4</sub>py][Tf<sub>2</sub>N] are almost similar and overlapping against one another. The absorption of CO<sub>2</sub> increases slightly as the alkyl side chain of the cation increases regardless of the type of the cation.

Figures 6 and 7 show the low pressure absorption of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] and [C<sub>12</sub>py][Tf<sub>2</sub>N], respectively, from (1.00 – 10.04) bar at 298.15K. The importance of studying other gases solubility in ionic liquids is to establish the selectivity of the ionic liquids towards different gas absorption in gas separations as well as to develop understanding on how different gas interacts with the ionic liquids. From the figures, CO<sub>2</sub> has the highest solubility in the ionic liquids followed by CH<sub>4</sub> and N<sub>2</sub>. For example, the mol fraction ratio of the solubility of CO<sub>2</sub>:CH<sub>4</sub>:N<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] at 10 bar and 298.15K is approximately 14.4:1.7:1.0 and 8.1:1.7:1.0 for [C<sub>12</sub>py][Tf<sub>2</sub>N] at the same pressure and temperature. These preliminary results indicate that there is a potential of the ionic liquids to be used to separate CO<sub>2</sub> from natural gas especially [C<sub>4</sub>py][Tf<sub>2</sub>N]. Table 2 shows the comparison of the Henry's law constant,  $K_H$  for the absorption of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> in the ionic liquids at temperature of 298.15K and in the pressure range of 1.00 – 10.04 bar. High  $K_H$  value indicates low solubility and vice versa.

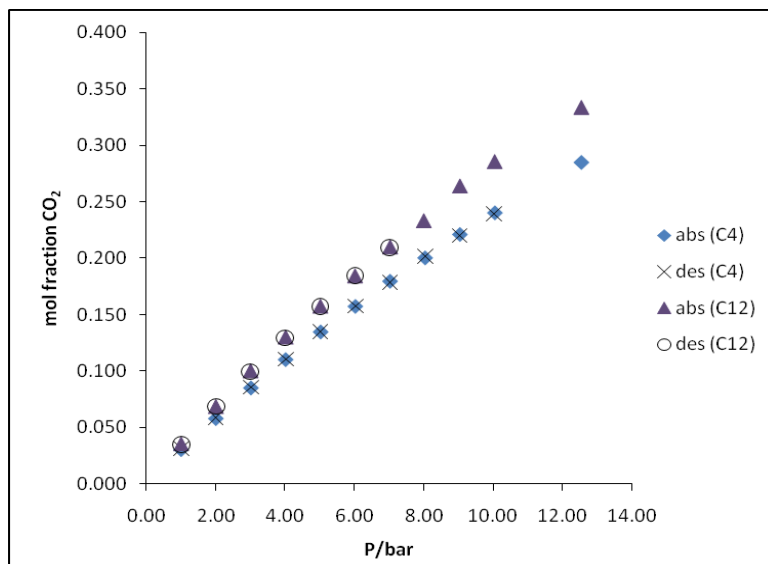


Figure 2: Plot of low pressure solubility of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] and [C<sub>12</sub>py][Tf<sub>2</sub>N] at 298.15K from (1.00 – 12.53) bar.: ♦ [C<sub>4</sub>py][Tf<sub>2</sub>N] absorption, × [C<sub>4</sub>py][Tf<sub>2</sub>N] desorption, ▲ [C<sub>12</sub>py][Tf<sub>2</sub>N] absorption, ○ [C<sub>12</sub>py][Tf<sub>2</sub>N] desorption.



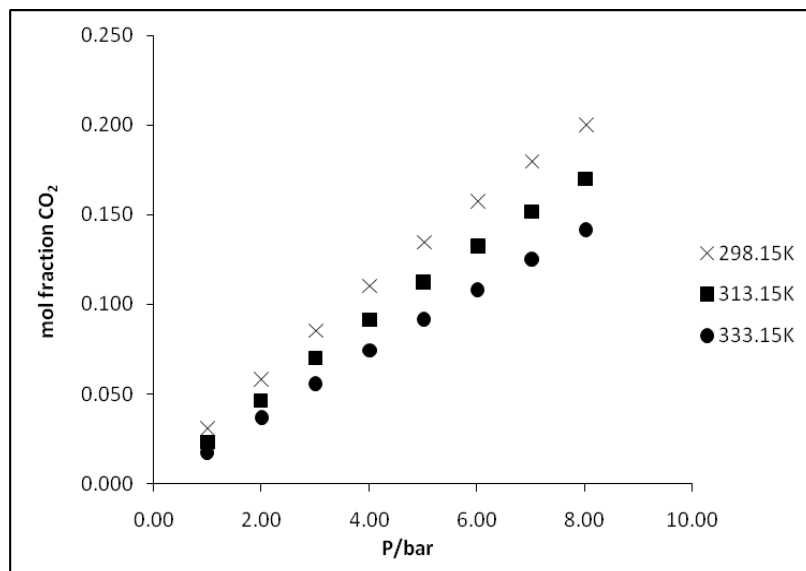


Figure 3: Plot of low pressure solubility of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] ,: × 298.15K, ■ 313.15K and ● 333.15K.

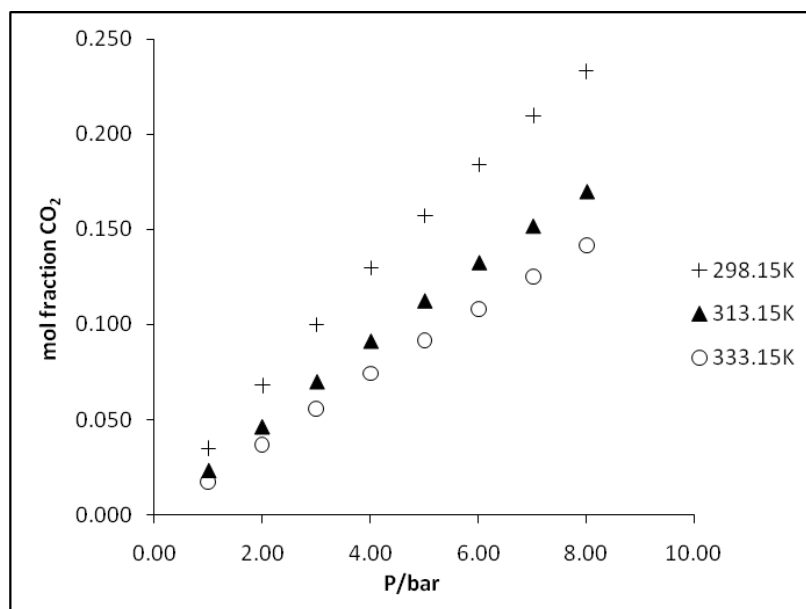


Figure 4: Plot of low pressure solubility of CO<sub>2</sub> in [C<sub>12</sub>py][Tf<sub>2</sub>N] ,: + 298.15K, ▲ 313.15K and ○ 333.15K.

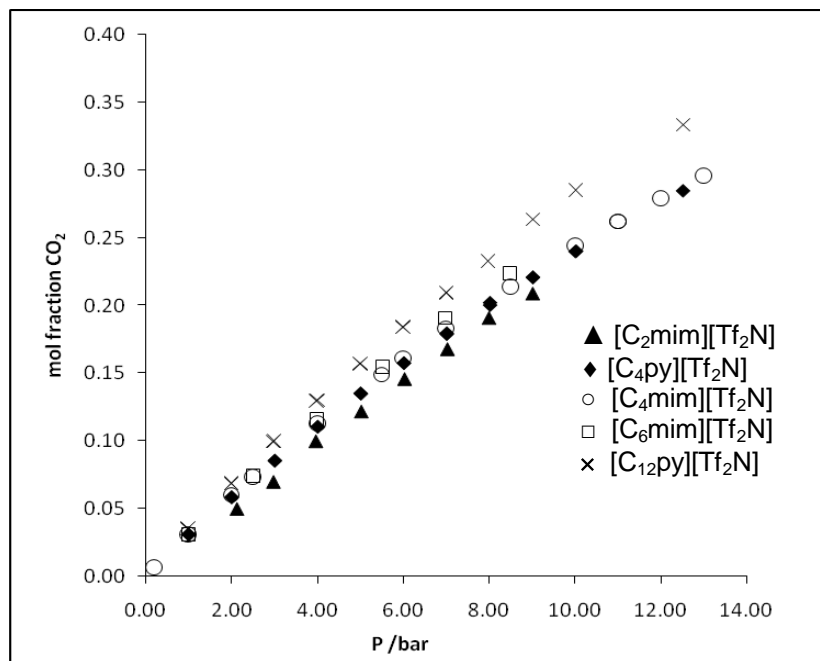


Figure 5: Comparison of experimental absorption of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] and [C<sub>12</sub>py][Tf<sub>2</sub>N] at 298.15K with [C<sub>2</sub>mim][Tf<sub>2</sub>N] [9], [C<sub>4</sub>mim][Tf<sub>2</sub>N] [8] and [C<sub>6</sub>mim][Tf<sub>2</sub>N] [19] from literature.: ▲ [C<sub>2</sub>mim][Tf<sub>2</sub>N], ◆ [C<sub>4</sub>py][Tf<sub>2</sub>N], ○ [C<sub>4</sub>mim][Tf<sub>2</sub>N], □ [C<sub>6</sub>mim][Tf<sub>2</sub>N] and × [C<sub>12</sub>py][Tf<sub>2</sub>N].

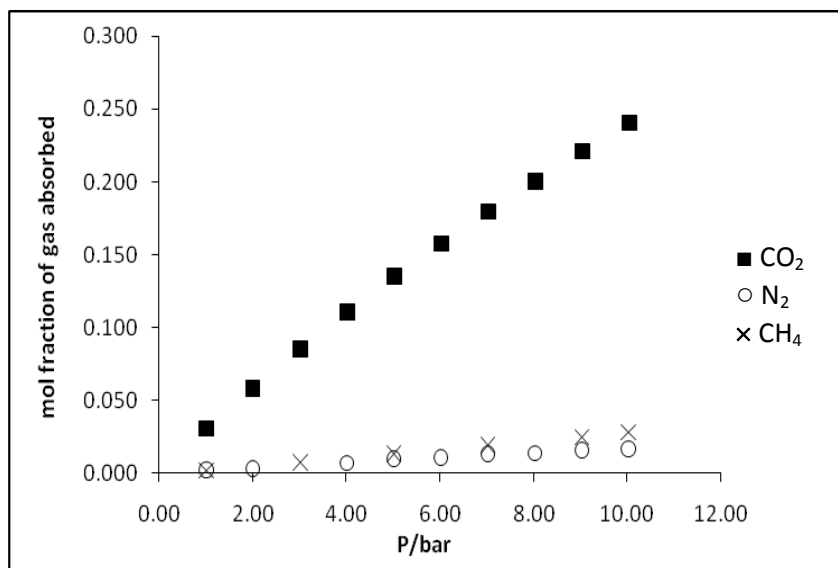


Figure 6: Comparison of absorption of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] from (1.00 – 10.04) bar at 298.15K.: ■ CO<sub>2</sub>, ○ N<sub>2</sub> and × CH<sub>4</sub>.

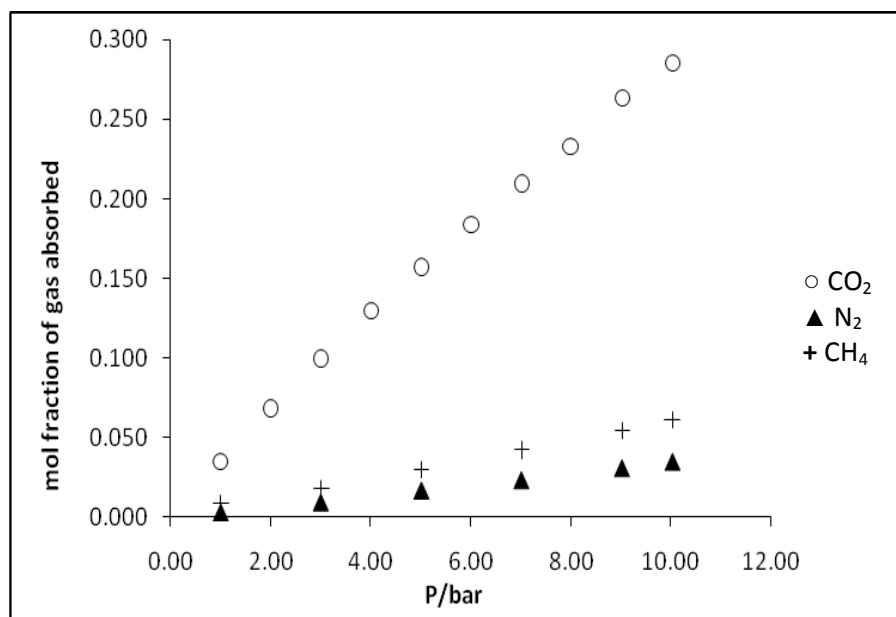


Figure 7: Comparison of absorption of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> in [C<sub>12</sub>py][Tf<sub>2</sub>N] from (1.00 – 10.03) bar at 298.15K.: ○ CO<sub>2</sub>, ▲ N<sub>2</sub> and + CH<sub>4</sub>.

Ionic liquid	$K_H$ (bar)		
	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
[C <sub>4</sub> py][Tf <sub>2</sub> N]	32.1	404.3	497.1
[C <sub>12</sub> py][Tf <sub>2</sub> N]	27.2	164.8	312.2

Table 2: Henry's law constants,  $K_H$  for the absorption of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> in the ionic liquids at temperature of 298.15K and in the pressure range of (1.00 – 10.04) bar.

## 5. CONCLUSIONS

The low pressure solubility of CO<sub>2</sub> in two pyridinium based ionic liquids has been measured at 298.15K, 313.15K and 333.15K and in the pressure of range up to 12.54 bar. In addition, the low pressure solubility of CH<sub>4</sub> and N<sub>2</sub> in the ionic liquids was measured at 298.15K and in the pressure range up to 10.03 bar. Increasing the pressure will increase the solubility of CO<sub>2</sub> while increasing the temperature will decrease the solubility of CO<sub>2</sub> in the ionic liquids. Changing the cation alkyl chain length has minor effect on the CO<sub>2</sub> absorbed by the ionic liquids. The comparison of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> absorption in the ionic liquids shows that the ionic liquids have high selectivity over CO<sub>2</sub> thus indicates that the ionic liquids have the potential to be used as a solvent to separate CO<sub>2</sub> from natural gas.

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## 7. LIST OF FIGURES

Figure 1: Structure of [C<sub>4</sub>py][Tf<sub>2</sub>N] (left) and [C<sub>12</sub>py][Tf<sub>2</sub>N] (right).

Figure 2: Plot of low pressure solubility of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] and [C<sub>12</sub>py][Tf<sub>2</sub>N] at 298.15K from (1.00 – 12.53) bar.: ♦ [C<sub>4</sub>py][Tf<sub>2</sub>N] absorption, × [C<sub>4</sub>py][Tf<sub>2</sub>N] desorption, ▲ [C<sub>12</sub>py][Tf<sub>2</sub>N] absorption, ○ [C<sub>12</sub>py][Tf<sub>2</sub>N] desorption.

Figure 3: Plot of low pressure solubility of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] ,: × 298.15K, ■ 313.15K and ● 333.15K.

Figure 4: Plot of low pressure solubility of CO<sub>2</sub> in [C<sub>12</sub>py][Tf<sub>2</sub>N] ,: + 298.15K, ▲ 313.15K and ○ 333.15K.

Figure 5: Comparison of experimental absorption of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] and [C<sub>12</sub>py][Tf<sub>2</sub>N] at 298.15K with [C<sub>2</sub>mim][Tf<sub>2</sub>N] [9], [C<sub>4</sub>mim][Tf<sub>2</sub>N] [8] and [C<sub>6</sub>mim][Tf<sub>2</sub>N] [19] from literature.: ▲ [C<sub>2</sub>mim][Tf<sub>2</sub>N], ♦ [C<sub>4</sub>py][Tf<sub>2</sub>N], ○ [C<sub>4</sub>mim][Tf<sub>2</sub>N], □ [C<sub>6</sub>mim][Tf<sub>2</sub>N] and × [C<sub>12</sub>py][Tf<sub>2</sub>N].

Figure 6: Comparison of absorption of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] from (1.00 – 10.04) bar at 298.15K.: ■ CO<sub>2</sub>, ○ N<sub>2</sub> and × CH<sub>4</sub>.

Figure 7: Comparison of absorption of CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> in [C<sub>12</sub>py][Tf<sub>2</sub>N] from (1.00 – 10.03) bar at 298.15K.: ○ CO<sub>2</sub>, ▲ N<sub>2</sub> and + CH<sub>4</sub>.

## 8. LIST OF TABLES

Table 1: Experimental density ( $\rho$ ) values of [C<sub>n</sub>py][Tf<sub>2</sub>N] at temperatures (293.15 – 353.15)K.

Table 2: Henry's law constants,  $K_H$  for the absorption of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> in the ionic liquids at temperature of 298.15K and in the pressure range of 1.00 – 10.04 bar.