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# Modeling of Solubility of CO<sub>2</sub> in 1-Butylpyridinium Bis(trifluoromethylsulfonyl)imide Ionic Liquid using UNIFAC

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**Abstract.** The solubility of CO<sub>2</sub> in 1-butylpyridinium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>py][Tf<sub>2</sub>N] ionic liquid has been determined using Magnetic Suspension Balance instrument at 298.15 K and in the pressures up to about 27 bar. A group contribution method, namely UNIFAC has been used to fit the experimental data. The interaction parameters of the model were estimated. The predicted CO<sub>2</sub> solubility data by the model shows good agreement with the experimental data.

**Keywords:** Ionic liquid, Pyridinium, CO<sub>2</sub>, UNIFAC.

**PACS:** 51.30.+i

## INTRODUCTION

Natural gas is used mainly as a fuel and also as a raw material for manufacturers such as in petrochemical industry. It is regarded as an environmentally friendly clean fuel compared to other fossil fuel [1]. However the presence of carbon dioxide (CO<sub>2</sub>) in natural gas lowers the fuel value of it. The most commonly used technique to remove CO<sub>2</sub> is by chemically absorbing CO<sub>2</sub> with aqueous alkanolamines [2]. However, there were few drawbacks in this technique such as degradation of the aqueous solution, high enthalpy of reaction for the chemical absorption of CO<sub>2</sub> in this solution and also corrosion and fouling problems of the process [3]. Ionic liquids which possess a number of unique properties such as high thermal stability and extremely low vapor pressure are currently 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 the CO<sub>2</sub>. To date, several ionic liquids were successfully applied in absorbing carbon dioxide under experimental conditions [4-7].

Before these new solvents can be used in separation processes, it is important to know the physical properties of the ionic liquids such as gas solubility, gas diffusion, viscosity, density etc. Other than that, it is important to know what properties or chemical structures of ionic liquids affect gas solubility and diffusion. For the right choice of the

selective solvent and for the development and design of separation processes, a reliable knowledge of the phase equilibrium behavior is required. For these purposes, understanding of the gas solubility or phase behavior of gas +ionic liquid is most important. In addition, there are a vast number of possible combinations of anions and cations for ionic liquids and therefore reliable predictive models would be highly desirable. Predictive models would allow the search for best-suited ionic liquid for a given separation process [8]. In this study, the solubility of CO<sub>2</sub> in 1-butylpyridinium bis(trifluoromethylsulfonyl)imide was determined at 298.15 K an pressures up to approximately 27 bar. The solubility data was modeled using a group contribution method i.e UNIFAC.

## METHODOLOGY

The methodology section is divided into experimental section and modeling section. The synthesis, structure and CO<sub>2</sub> solubility measurement are described in the experimental section. Meanwhile the modeling of the CO<sub>2</sub> solubility data is presented in the modeling section.

## Experimental

The ionic liquid [C<sub>4</sub>py][Tf<sub>2</sub>N] has been synthesized using 2-step method, alkylation and ion exchange reactions. The synthesis and the thermophysical properties of the ionic liquid have been reported

previously [9]. The structure of the ionic liquid is shown in Figure 1.

A magnetic suspension balance (MSB) from Rubotherm Präzisionsmesstechnik GmbH, rated up to 150 bar and 250°C, was used to measure the solubility of CO<sub>2</sub> in the ionic liquid. The balance, which has the mass precision of ±20 µg, 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 weight change of the sample upon absorption of the gas.

In the solubility experiment, the ionic liquid sample, about 1 g, was placed in a sample basket and loaded in the absorption chamber. The sample was then evacuated at 100°C at 10<sup>-3</sup> mbar (Pfeiffer model DUO5) to remove any water, solvents or dissolved gases for at least 24 hours or until the weight remains constant. The temperature of the absorption chamber is controlled by a circulator (Julabo model F25-ME) with an accuracy of ±0.1°C. The chamber was then pressurized with CO<sub>2</sub> gas (Malaysia Oxygen Berhad, purity >99.99%) at constant temperature and the weight was monitored as the gas dissolved into the sample. The gas was dried in a gas dryer filled with molecular sieve prior entering the absorption chamber. Once the weight reached a constant value, it was maintained at that condition for at least 2 hours to ensure complete equilibration before the pressure of the system was increased to other value. The desorption isotherm was also measured by incrementally evacuating the gas from the system.

The mass of the gas dissolved in the ionic liquid,  $w_g$ , is calculated using the following equation:

$$w_g = w_l(P, T) - w_{(SC+S)} + \rho_g(P, T) \cdot (V_{SC} + V_S) \quad (1)$$

where  $w_l(P, T)$  is the corrected weight of the balance at pressure,  $P$  and temperature,  $T$ ,  $w_{(SC+S)}$  is the weight of sample container and sample.  $\rho_g$  is the gas density, (g.cm<sup>-3</sup>) and  $V_{SC}$  and  $V_S$  (cm<sup>3</sup>) are the volumes of the sample container and sample, respectively.

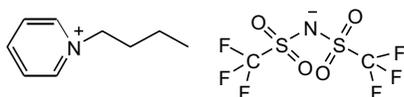


FIGURE 1. Structure of [C<sub>4</sub>py][Tf<sub>2</sub>N].

## Modeling

For a gas solute 2 dissolves in liquid phase 1, the gas phase fugacity becomes equal to the liquid phase fugacity at equilibrium [10,11].

$$f_2^L = f_2^G \quad (2)$$

Assuming that the gas phase is ideal and the fugacity coefficient is close to unity, then the gas phase fugacity is estimated using the following equation:

$$f_2^G = y_2 P \quad (3)$$

where  $P$  is the total pressure and  $y_2$  is the mole fraction of the gas solute in the gas phase. The mole fraction of the gas in the gas phase is considered to be equal to unity for non-volatile liquid solvents such as ionic liquids. Liquid phase non-ideality can be determined using activity coefficient calculations thus the fugacity of the gas solute in the solvent can be written as

$$f_2^L = x_2 \gamma_2 f_2^\circ \quad (4)$$

where  $x_2$  and  $\gamma_2$  are the mol fraction and the activity coefficient of gaseous 2 in solvent 1, respectively.  $f_2^\circ$  represents the property of a hypothetical pure liquid whenever the temperature is greater than the critical temperature of the gas.  $f_2^\circ$  cannot be determined experimentally [12] hence the expression is modified into estimating Henry's law constant for a reference solvent.

$$f_2^\circ = \frac{H_{2,r}}{\gamma_{2,r}^\infty} \quad (5)$$

In this equation,  $\gamma_{2,r}^\infty$  is the infinite dilution activity coefficient of the gas in the reference solvent and  $H_{2,r}$  is the Henry's law constant of the gas in the reference solvent. The mole fraction of the solute gas in the ionic liquid solvent can then be calculated.

$$x_2 = \frac{y_2 P}{H_{2,r} (\gamma_2 / \gamma_{2,r}^\infty)} \quad (6)$$

The activity coefficient was calculated using UNIFAC model. The UNIFAC equation for the activity coefficient of component  $i$  can be expressed in the following form [13]:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (7)$$

where  $\ln \gamma_i^C$  represents the combinatorial part and  $\ln \gamma_i^R$  accounts for the residual part of the model. The combinatorial part is given by the following equation [14]:

$$\ln \gamma_i^C = \frac{\ln \psi_i}{x_i} + 1 - \frac{\psi_i}{x_i} - \frac{1}{2} z q_i \left( \frac{\ln \varphi_i}{\theta_i} + 1 - \frac{\varphi_i}{\theta_i} \right) \quad (8)$$

with

$$\psi_i = x_i r_i^{2/3} / \sum_j x_j r_j^{2/3} \quad (9)$$

$$\varphi_i = x_i r_i / \sum_j x_j r_j \quad (10)$$

$$\theta_i = x_i q_i / \sum_j x_j q_j \quad (11)$$

and

$$r_i = \sum_k v_k^{(i)} R_k ; q_i = \sum_k v_k^{(i)} Q_k \quad (12)$$

where  $R_k$  and  $Q_k$  are the van der Waals group parameters.

The residual part of the UNIFAC equation is given as follows:

$$\ln \gamma_i^R = \sum_k v_{ki} \left( \ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \quad (13)$$

$$\ln \Gamma_k = Q_k \left[ \begin{array}{l} 1 - \ln \left( \sum_m \theta_m \Psi_{mk} \right) \\ - \sum_m \left( \theta_m \Psi_{km} / \sum_n \theta_n \Psi_{nm} \right) \end{array} \right] \quad (14)$$

where

$$\theta_m = Q_m x_m / \sum_n Q_n x_n \quad (15)$$

$$x_m = \frac{\sum_j v_{mj} x_j}{\sum_j \sum_n v_{nj} x_j} \quad (16)$$

and

$$\Psi_{nm} = \exp(-a_{nm}/T) \quad (17)$$

$\Gamma_k$  is the group residual activity coefficient,  $\Gamma_k^{(i)}$  is the residual activity coefficient of group  $k$  in the reference solution containing only molecules of type  $i$  and  $a_{nm}$  is the group interaction parameter for the interaction between groups  $m$  and  $n$  where  $a_{nm} \neq a_{mn}$ . In this work, the ionic liquid is decomposed in two main parts, one part consists of the alkyl chain group and the other part consists of the combination of pyridine group and the Tf<sub>2</sub>N anion group. CO<sub>2</sub> is treated as one group. The group interaction parameters were estimated using experimental data using the following objective function,  $OF$ :

$$OF = \sum_n \left[ \ln(\gamma_2 / \gamma_{2,r}^\infty)_{\text{exp}} - \ln(\gamma_2 / \gamma_{2,r}^\infty)_{\text{calc}} \right]^2 \quad (18)$$

where  $n$  is the number of data points and  $\gamma_2$  is the activity coefficient of CO<sub>2</sub> calculated by using the UNIFAC equations. The new estimated binary interaction parameters are presented in Table 1.

**TABLE 1.** Group interaction parameters for UNIFAC.

Group $n$ – Group $m$	$a_{nm}$ (K)	Reference
CH <sub>3</sub> – pyridine[Tf <sub>2</sub> N]	327.30	[15]
pyridine[Tf <sub>2</sub> N] – CH <sub>3</sub>	301.96	[15]
CH <sub>3</sub> – CO <sub>2</sub>	165.72	[16]
CO <sub>2</sub> – CH <sub>3</sub>	209.10	[10]
pyridine[Tf <sub>2</sub> N] – CO <sub>2</sub>	248.36	This work
CO <sub>2</sub> – pyridine[Tf <sub>2</sub> N]	-202.85	This work

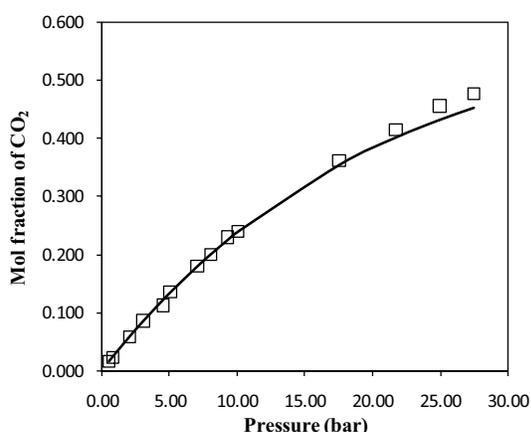
## RESULTS AND DISCUSSION

Figure 2 shows the results of CO<sub>2</sub> solubility in [C<sub>4</sub>py][Tf<sub>2</sub>N] at 298.15 K and pressures up to 27.48 bar. The plots show that the solubility of CO<sub>2</sub> in the ionic liquids increases with the pressure of CO<sub>2</sub>. From the results, the mol fraction of CO<sub>2</sub> absorbed in the ionic liquids increases with pressure, reaching to 0.48 mol fraction at 27.48 bar at 298.15 K. Based on the Henry's law, the solubility of a gas in a liquid is proportional to the partial pressure of the gas above the surface of the liquid [17]. Linear relationship was obtained between the pressure and the amount of CO<sub>2</sub> absorbed in the ionic liquid below approximately 10 bar. The plot exhibits nonlinear trend as the pressure increases and exceeds approximately 10 bar.

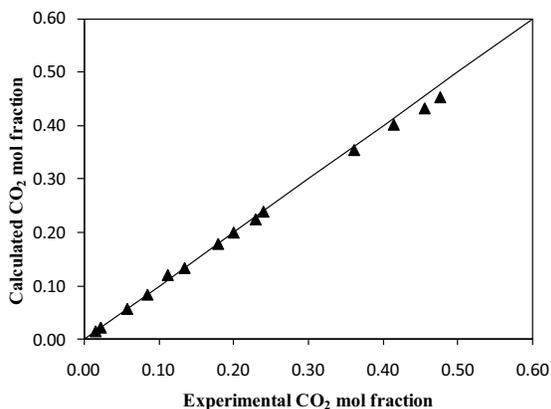
The UNIFAC prediction for the CO<sub>2</sub> solubility in [C<sub>4</sub>py][Tf<sub>2</sub>N] at 298.15 K and pressures below 28 bar was satisfactory as displayed in Figure 2 with the

average percentage deviation of 0.25%. The deviation is calculated using Equation (19). Meanwhile, the comparison of the experimental and predicted CO<sub>2</sub> mol fraction using UNIFAC model for [C<sub>4</sub>py][Tf<sub>2</sub>N] at 298.15 K and pressures below 28 bar is shown in Figure 3. On the basis of obtained deviation, it can be concluded that UNIFAC model can be satisfactorily used to predict the CO<sub>2</sub> – [C<sub>4</sub>py][Tf<sub>2</sub>N] solubility data at given operating pressure and temperature.

$$dev = \frac{1}{N} \sum_{i=1}^N |x_i^{cal} - x_i^{exp}| \times 100 \quad (19)$$



**FIGURE 2.** Structure of [C<sub>4</sub>py][Tf<sub>2</sub>N]. Solubility of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] at 298.15 K in the pressure range up to 27 bar: □ [C<sub>4</sub>py][Tf<sub>2</sub>N] experimental data, (—) modeled with UNIFAC.



**FIGURE 3.** Parity plots of the UNIFAC model prediction of the CO<sub>2</sub> solubility in [C<sub>4</sub>py][Tf<sub>2</sub>N] 298.15 K and pressure below 28 bar.

## CONCLUSION

The solubility of CO<sub>2</sub> in [C<sub>4</sub>py][Tf<sub>2</sub>N] ionic liquid has been measured at 298.15 K and in the pressure range up to about 28 bar. The results show that the ionic liquid is capable of absorbing CO<sub>2</sub> at room temperature. Increasing the pressure will increase the amount of CO<sub>2</sub> absorbed. UNIFAC model has been used to predict the solubility data. New group interaction parameters were estimated based on experimental data. On the basis of percent deviation calculation, it is concluded that the model can satisfactorily predict the solubility data.

## ACKNOWLEDGEMENTS

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