



# MOLECULAR SIMULATION STUDY OF CO<sub>2</sub> ADSORPTION IN IONIC LIQUID IMPREGNATED CuBTC

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**RESUMO:** Neste trabalho, analisou-se a adsorção de CO<sub>2</sub> na estrutura metalorgânica (MOF) CuBTC impregnada com um líquido iônico através de simulação molecular utilizando o método de Monte Carlo. O líquido iônico (LI) utilizado para impregnação no suporte CuBTC foi o hexafluorofosfato de 1-butil-3-metilimidazólio ([bmim][PF<sub>6</sub>]). Foram realizadas simulações de impregnação usando o ensemble Canônico (NVT) para gerar estruturas impregnadas com diferentes quantidades de LI. Assim, simulações de adsorção de CO<sub>2</sub> nas estruturas geradas foram realizadas utilizando o ensemble Grande Canônico ( $\mu$ VT) para avaliar a influência do carregamento de LI na estrutura da CuBTC sobre a capacidade de adsorção do CO<sub>2</sub>. Observou-se que a presença de LI em várias concentrações provocou um aumento da capacidade adsorptiva à baixas pressões (entre 0 e 3 bar) em relação ao suporte sem LI. Este resultado é atribuído não só a afinidade entre o LI e o CO<sub>2</sub>, uma vez que ambos são moléculas polares, mas também à geração de sítios mais fortes de adsorção pela presença do LI, o que propicia uma maior retenção de CO<sub>2</sub> a baixas pressões.

**PALAVRAS-CHAVE:** simulação molecular; CuBTC; impregnação; líquido iônico; CO<sub>2</sub>.

**ABSTRACT:** In this work, we analyzed the adsorption of CO<sub>2</sub> in a CuBTC metal-organic framework functionalized with ionic liquids (ILs) by means of Monte Carlo molecular simulation. The ionic liquid used to impregnate the CuBTC matrix was the 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]). The addition of the IL molecules into the CuBTC structures was carried out by using a Canonical Monte Carlo ensemble (NVT) and IL-impregnated structures were generated for several IL loads. Finally, CO<sub>2</sub> adsorption simulations were performed on the structures using the Grand Canonical ensemble ( $\mu$ VT) in order to study the effect of IL increasing loads on the CuBTC structure over CO<sub>2</sub> adsorption isotherms. It could be observed that the presence of IL in a wide range of concentration has improved the CO<sub>2</sub> adsorption capacity at low pressures (from 0 to 3 bar) if compared to the MOF without IL. This result is attributed not only to the affinity between the IL and CO<sub>2</sub>, since these are both polar molecules, but also to the generation of stronger adsorption sites by presence of IL, which leads to a higher retention of CO<sub>2</sub> at lower pressure.

**KEYWORDS:** molecular simulation, CuBTC, ionic liquids, CO<sub>2</sub>, adsorption.

## 1. INTRODUCTION

The capture and separation of CO<sub>2</sub> gas mixtures consists of an important subject to be studied and involves both scientific and environmental interests.

Carbon dioxide is constantly being generated and absorbed in nature and its excess is one of the main factors that may

accentuate the greenhouse effect in the atmosphere. Although methane and chlorofluorocarbons have a larger greenhouse effect per mass unit of gas, the carbon dioxide is a major contributor due to the amount present in the atmosphere, accounting for 60% of global warming effects (Yamasaki, 2003). The purification process of natural gas is another scenario in which the separation of



CO<sub>2</sub> is important. The natural gas reserves are generally contaminated with volumetric proportions up to 70% CO<sub>2</sub> and N<sub>2</sub>. On the other hand, the specifications for gas transport in pipelines require CO<sub>2</sub> concentrations below 2-3% (Baker, 2002). CO<sub>2</sub> reduces the energetic density of natural gas and also is corrosive in the presence of water (Ghoufi et al., 2009).

Several separation technologies have been studied aiming at CO<sub>2</sub> capture, including: absorption in amines, separation membranes, adsorption and cryogenic separation (Ebner and Ritter, 2009). The absorption using monoethanolamine (MEA) is the most commonly used method and has been widely applied in the natural gas industry for over 60 years (Yang et al., 2008). This method has several disadvantages, however, such as high energy consumption for regenerating the liquid, corrosion of equipment and emissions of volatile components. In this context, Ionic Liquids have been proposed as a promising alternative to traditional volatile solvents because of their low volatility and of other interesting properties (Ramdin et al. 2012). Ionic liquids (ILs) are defined as salts in liquid form and have a melting point below 373 K and are constituted by a combination of different cations and anions (Maggin, 2009).

The application of ionic liquids in industrial separation processes is limited by its high cost (Ramdin et al., 2012). One possible solution to this problem is to impregnate or functionalize ionic liquids in porous media (Vincent-Luna et al., 2013). In this context, metal-organic frameworks (MOFs) have been proposed as potential adsorbents due to its high adsorption capacity of CO<sub>2</sub> and adjustability of their textural properties and surface chemistry (Xu et al, 2009; Chen et al, 2011; Gupta et al., 2011). Vincent-Luna et al. (2013) investigated by molecular simulation the adsorption of CO<sub>2</sub> in MOF CuBTC impregnated with different ionic liquids and found that the adsorption capacity of CO<sub>2</sub> at low pressures is increased.

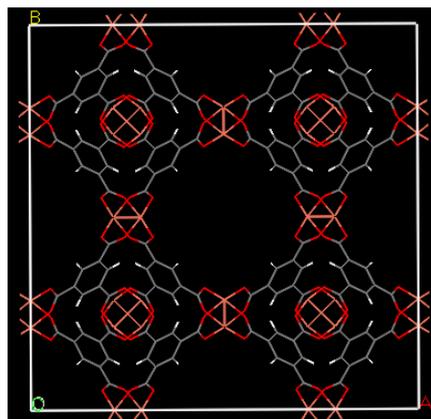
In this work, molecular simulation studies of CO<sub>2</sub> adsorption were conducted in

CuBTC modified by impregnation with ionic liquid. The ionic liquid (IL) chosen for impregnating the support was hexafluorophosphate 1-butyl-3-methylimidazolium, since it is a relatively well studied LI. The effect of the concentration of IL presence on the adsorption capacity of the system MOF-LI was analyzed.

## 2. METHODS AND MODELS

Monte Carlo simulations were performed using Canonical and Grand Canonical ensembles. The canonical ensemble (NVT) was used for the addition of cations and anions (in equal proportion) of LI in the unit cell of CuBTC. This allows molecules to be positioned in the preferential sites of the CuBTC unit cell so that the resulting structure is energy-minimized. Subsequently, CO<sub>2</sub> adsorption isotherms were simulated using the Grand Canonical ensemble ( $\mu$ VT), most suitable for systems where phase transfer occurs.

The unit cell of CuBTC was constructed from crystallographic data (XRD) (Chui et al., 1999) using Visualiser module (Accelrys Inc. – EUA) (see Figure 1) and the atomic charges were obtained from Yang and Zhong (2006).



**Figure 1.** CuBTC unit cell structure. The carbon atoms are plotted in gray, the hydrogen atoms in white, and the oxygen and the copper atoms are in red and orange, respectively.

The CuBTC structure has a cubic and crystalline unit cell described by the F3-3m space group. As shown in Figure 1, the structure is composed by clusters of

$\text{Cu}_2(\text{COO})_4$  with copper dimers linked to the benzene-1,3,5-tricarboxylate tridentate ligands, forming a three-dimensional structure with two cavities: one central octahedral cavity with quadratic section diameter of 9 Å and eight side tetrahedral cavities with quadratic section diameter of 5 Å, which are connected to the main channels by triangular windows of 3.5 Å diameter (Wang et al., 2008).

The Lennard-Jones parameters that describe the structure of energetic interactions CuBTC were taken from the generic DREIDING force field (Mayo et al. 1990), with the exception of copper atoms, whose parameters were obtained from the UFF (Rappe et al. 1992) (see Table 1).

**Table 1.** Lennard-Jones parameters and charges for CuBTC cell.

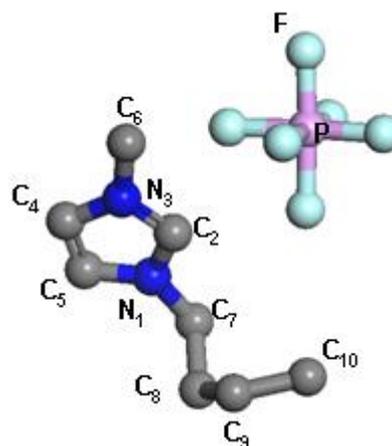
Atom	$\epsilon/\text{K}_B(\text{K})$	$\sigma (\text{Å})$	Charge ( $e$ )
Cu	2.518	3.114	1.248
O	48.190	3.030	-0.624
H	7.650	2.850	0.156
C <sub>1</sub>	47.860	3,470	0.494
C <sub>2</sub>	47.860	3,470	0.130
C <sub>3</sub>	47.860	3,470	-0.156

The molecular model of the ionic liquid in question, [bmim][PF<sub>6</sub>], is shown in Figure 2. In order form the ionic liquid, the cation 1-butyl-3-methyl-imidazolium chloride (bmim) is combined with the hexafluorophosphate anion (PF<sub>6</sub>). The cation is composed of flexible and methyl butyl groups attached to an aromatic ring, which is modeled as a rigid structure. The geometry and parameters were obtained from Shah and Maggin (2004).

Table 2 lists the force field parameters for intermolecular energy potentials used in the modeling of IL. Atoms are numbered according to the distance to the nitrogen atom of the aromatic ring.

**Table 2.** Lennard-Jones parameters and charges for [bmim][PF<sub>6</sub>] sctstructure.

Atom	$\epsilon/\text{K}_B(\text{K})$	$\sigma (\text{Å})$	Charge ( $e$ )
P	2.518	3.114	+1.248
F	48.190	3.030	-0.624
N <sub>1</sub>	3.250	0.710	+0.111
N <sub>3</sub>	3.250	0.710	+0.133
C <sub>2</sub>	3.880	0.443	+0.233
C <sub>4</sub>	3.880	0.443	+0.040
C <sub>5</sub>	3.880	0.443	-0.010
C <sub>6</sub>	3.775	0.865	+0.183
C <sub>7</sub>	3.905	0.493	+0.195
C <sub>8</sub>	3.905	0.493	+0.066
C <sub>9</sub>	3.905	0.493	+0.128
C <sub>10</sub>	3.905	0.732	-0.043



**Figure 2.** Molecular representation of the Ionic Liquid [bmim][PF<sub>6</sub>].

With the assumption of flexible parts in the LI cation, it is also necessary to introduce force field parameters so that intramolecular interactions are accounted.

We considered the energies associated with the torsions between nitrogen and carbon



8 of the cation. Equation 1 describes the interaction potential for torsion.

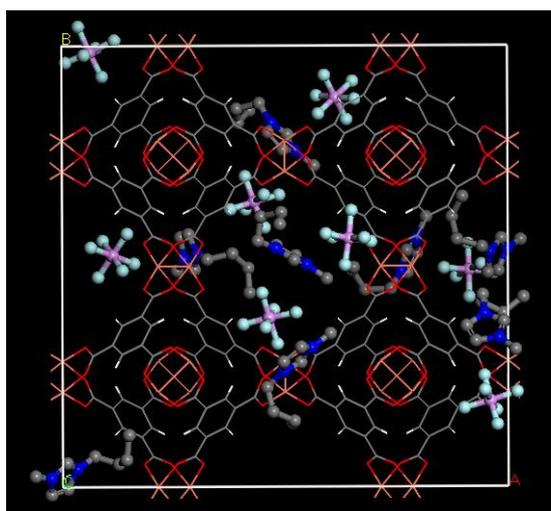
$$v(\phi) = v_0 + \frac{1}{2}v_1(1 + \cos(\phi)) + \frac{1}{2}v_2(1 - \cos(2\phi)) + \frac{1}{2}v_3(1 + \cos(3\phi)) \quad (1)$$

The parameters required for Equation 1 are shown below in Table 3.

**Table 3.** Torsion parameters for [bmim][PF<sub>6</sub>].

Dihedral Angle	V <sub>1</sub> (kJ/mol)	V <sub>2</sub> (kJ/mol)	V <sub>3</sub> (kJ/mol)
C <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub> -C <sub>10</sub>	5,89	-1,13	13,17
N <sub>1</sub> -C <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub>	11,41	0,96	2,05
C <sub>2</sub> -N <sub>1</sub> -C <sub>7</sub> -C <sub>8</sub>	-5,85	-1,80	0
C <sub>5</sub> -N <sub>1</sub> -C <sub>7</sub> -C <sub>8</sub>	-5,85	-1,80	0

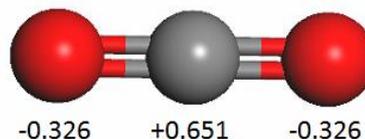
The CuBTC unit cell loaded with eight molecules of [bmim][PF<sub>6</sub>] ionic liquid is shown on Figure 3.



**Figure 3.** Impregnated CuBTC unit cell.

Finally, the CO<sub>2</sub> molecule (Figure 4) was modeled as a rigid molecule with three sites of interactions with charges centered on each

atom (Vishnyakov et al. 1999), the parameters used are described in Table 4.



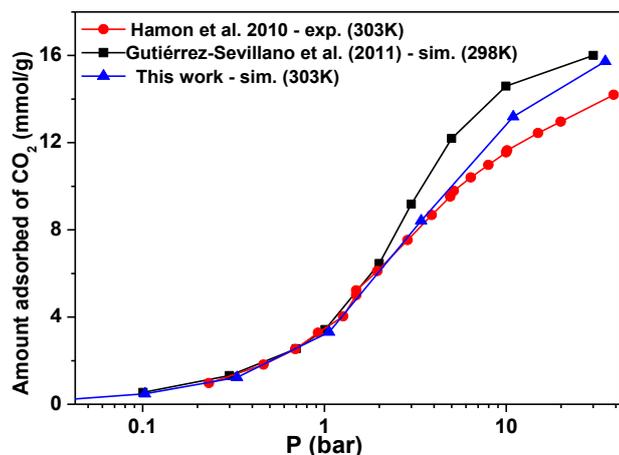
**Figure 4.** Representation of the carbon dioxide molecule and its charge.

**Table 4.** Lennard-Jones parameters and charges for CO<sub>2</sub>.

Atom	$\epsilon/K_B(K)$	$\sigma$ (Å)	Charge (e)
C	28,129	2,757	+0,651
O	80,507	3,033	-0,326

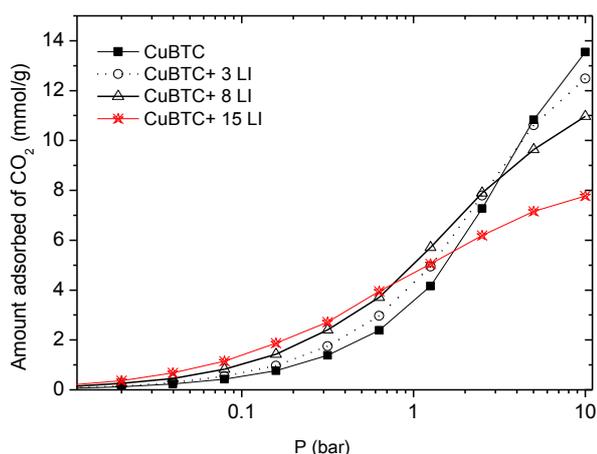
### 3. RESULTS

Initially, the models and parameters were validated by comparison with experimental data of simulated CO<sub>2</sub> adsorption isotherms at the same temperature. Figure 4 shows the results of the validation of the force field. Small discrepancy is seen in the comparison between the data obtained in the simulation and experimental data reported (Hamon et al, 2010; Gutiérrez-Sevillano et al, 2011). However, at high pressures, simulated isotherms typically show higher adsorption capacity than the experimental isotherm. This can be explained by fact that molecular simulation uses a perfect crystalline structure while the quality of the experimental samples depends on the synthesis and regeneration conditions, which can result in significant changes in the crystalline structure of the material.



**Figure 5.** CO<sub>2</sub> adsorption isotherms on CuBTC.

The analysis of the presence of ionic liquid in the MOF cell was performed by simulation of CO<sub>2</sub> adsorption in the impregnated structures. Several modified structures were generated with LI concentrations varying from 3, 8 and 15 molecules per unit cell of CuBTC. Figure 6 shows the results obtained by performing simulations of CO<sub>2</sub> adsorption in these structures. Here, it is observed that the presence of IL has increased the amount of adsorbed CO<sub>2</sub> in the range of 0 to about 3 bar at all concentrations of IL studied.



**Figure 6.** CO<sub>2</sub> adsorption isotherms at 298K on modified CuBTC for different IL concentrations

For industrial CO<sub>2</sub> capture processes which are commonly performed at lower

pressures, such as the removal of carbon dioxide from flue gas, it is interesting that the adsorption capacity is grown as high as possible at lower pressure ranges. This increase was observed for all samples impregnated. The increase in adsorption capacity can be explained by the combination of the size and geometry of the adsorbate, which tends to be adsorbed on smaller sites, and by the polar nature of the ionic liquid which is located in the larger pores. Therefore, smaller size and high polarizability of the CO<sub>2</sub> molecule, imply that it is easier to be "dissolved" in ionic medium.

The energy parameters of the cation also contribute to a larger amount of adsorbed gas since the carbon atoms of the [bmim] have values of  $\epsilon/K_B$  larger than the CuBTC carbon atoms, thus strengthening the energetic gas-solid interactions.

It is noted in Figure 5 that up to pressure of approximately 0.7 bar, the sample loaded with 15 IL molecules has showed the highest adsorption capacity. In sequence, for pressures between 0.7 and 3 bar, the samples impregnated with 8 IL molecules per unit cell sample had greater adsorption capacity, thus proving it to be the optimum concentration of the ionic liquid at a higher pressure range. Also in Figure 6, it is observed that above 3 bar, there is a reduction in the adsorption capacity of the impregnated material. This may be caused by steric obstruction created by the presence of LI in the structure of CuBTC, which now occupies the active adsorption sites and therefore reduces the volume available for gas.

## 4. CONCLUSION

CO<sub>2</sub> adsorption on CuBTC impregnated with ionic liquid at different concentrations was evaluated by molecular simulation using the Monte Carlo method. Molecular simulations using previously validated force fields showed that the impregnation of CuBTC with ionic liquids increased the adsorption capacity of CO<sub>2</sub> at low pressures. This result



leads to higher values of selectivity for CO<sub>2</sub> adsorption on impregnated structures comparing to the CuBTC matrix. The highest adsorption capacity for structures impregnated with the ionic liquid can be attributed to their polar character, making the CO<sub>2</sub> molecule is more easily "dissolved" in ionic medium.

## 5. REFERENCES

- BAKER, R.W. Future Directions of Membrane Gas Separation Technology. *Ind. Eng. Chem. Res.*, v. 41(6), p. 1393-1411, 2002.
- CHEN, Y.; HU, Z.; GUPTA, K. M.; JIANG, J. Ionic Liquid/Metal-Organic Framework Composite for CO<sub>2</sub> Capture: A Computational Investigation. *J. Phys. Chem. C*, v. 115, p. 21736–21742, 2011.
- CHUI, S.S.Y.; LO, S.M.F.; CHARMANT, J.P.H.; ORPEN, A.G.; WILLIAMS, I.D. A chemically functionalizable nanoporous material [Cu<sub>3</sub>(TMA)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>. *Science*, v. 283, p. 269-302, 1999.
- EBNER, A.D.; RITTER, J. A. State-of-the-art Adsorption and Membrane Separation Processes for Carbon Dioxide Production from Carbon Dioxide Emitting Industries. *Separation Science and Technology*, v. 44, p. 1273-1421, 2009.
- GHOUFI, A.; GABEROVA, L.; ROUQUEROL, J.; VICENT, D.; LLEWELLYN, P.L.; MAURIN, G. Adsorption of CO<sub>2</sub>, CH<sub>4</sub> and their binary mixture in Faujasite NaY: A combination of molecular simulations with gravimetry–manometry and microcalorimetry measurements. *Microporous and Mesoporous Materials*, v. 119, p. 117–128, 2009.
- GUTIÉRREZ-SEVILLANO, J.J.; CARO-PÉREZ, A.; DUBBELDAMB, D.; CALERO, S. Molecular simulation investigation into the performance of Cu–BTC metal–organic frameworks for carbon dioxide–methane separations. *Phys. Chem. Chem. Phys.*, v. 13, p. 20453–20460, 2011.
- GUPTA, K. M.; CHEN, Y.; HU, Z.; JIANG, J. Metal-Organic Framework Supported Ionic Liquid Membranes for CO<sub>2</sub> Capture: Anion Effects. *Phys. Chem. Chem. Phys.*, v. 14, p. 5785–5794, 2012.
- HAMON, L.; JOLIMAITRE, E.; PIRNGRUBER, G. D. CO<sub>2</sub> and CH<sub>4</sub> Separation by Adsorption Using Cu-BTC Metal-Organic Framework, *Ind. Eng. Chem. Res.* v. 49, p. 7497–7503, 2010.
- MAGINN, E. J. Molecular simulation of ionic liquids: current status and future opportunities *J. Phys.: Condens. Matter*, v. 21, 373101 (17pp), 2009.
- MAYO, S.; OLAFSON, B. D.; GODDARD III, W. A. DREIDING: A Generic Force Field for Molecular Simulations. *J. Phys. Chem.*, v. 94, p. 8897-8909, 1990.
- RAMDIN, M., LOSS, T.W.; VLUGT, T.J.H. State-of-the-Art of CO<sub>2</sub> Capture with Ionic Liquids, *Ind. Eng. Chem. Res.* v. 51, 8149–8177, 2012.
- RAPPÉ, A. K.; CASEWIT, C. J.; COLWELL, K. S.; GODDARD III, W. A.; SKIFF, W. M. UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *J. Am. Chem. Soc.*, v. 114, p. 10024-10035, 1992.
- SHAH, J. K.; MAGINN, E. J. A Monte Carlo simulation study of the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate: liquid structure, volumetric properties and infinite dilution solution thermodynamics of CO<sub>2</sub>, *Fluid Phase Equilibria*, v. 222–223, p.195–203, 2004.
- VICENT-LUNA, J.M.; ANTA, J.A.; CALERO, S. Effect of Room-Temperature Ionic Liquids on CO<sub>2</sub> Separation by a Cu-BTC

Metal–Organic Framework, *J. Phys. Chem. C*, v.117, p.20762–20768, 2013.

VISHNYAKOV, A.; RAVIKOVITCH, P. I.; NEIMARK, A. V. Molecular level models for CO<sub>2</sub> sorption in nanopores. *Langmuir*, v. 15, p. 8736-8742, 1999.

WANG, SANYUE; QINGYUAN YANG, CHONGLI ZHONG. Adsorption and separation of binary mixtures in a metal-organic framework Cu-BTC: A computational study. *Separation and Purification Technology* v. 60, p.30–35, 2008.

XU, L.; YAN, S.; CHOI, E.-Y.; LEE, J. Y.; KWON, Y.-U. Product Control by Halide Ions of Ionic Liquids in the Ionothermal Syntheses of Ni-(H)Btc Metal-Organic Frameworks. *Chem. Commun.* p.3431–3433, 2009.

YAMASAKI, A; An overview of CO<sub>2</sub> mitigation options for global warming – Emphasizing CO<sub>2</sub> sequestration options. *Journal of Chemical Engineering of Japan*, v.36(4), p.361–375, 2003.

YANG, H.; XU, Z.; FAN, M.; GUPTA, R.; SLIMANE, R. B.; BLAND, A. E.; WRIGHT, I. Progress in carbon dioxide separation and capture: A review. *Journal of Environmental Sciences*, v.20, p.14 – 27, 2008.

YANG QY, ZHONG CL. Electrostatic-field-induced enhancement of gas mixture separation in metal-organic frameworks: a computational study. *ChemPhysChem.* v.7, p.1417–1421, 2006.