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Capture of CO_2 in carbon nanotube bundles supported with room-temperature ionic liquids: A molecular simulation study

Yongping Zeng [a,*], Kai Li [a], Qingyu Zhu [b], Jilong Wang [a], Yanan Cao [a], Shengjie Lu [a]

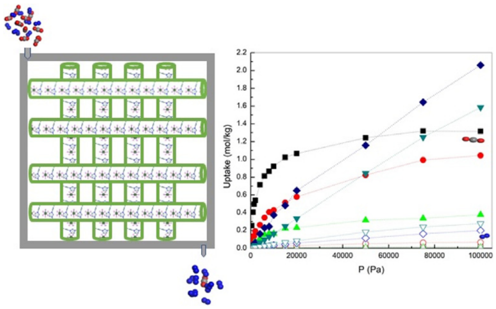
[a] *College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China*
[b] *Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge CB2 3RA, UK*

HIGHLIGHTS

- Introduction of ionic liquids into the channels of CNTs significantly enhances the adsorption of CO_2.
- [Bmim][PF_6]@CNTs composites show the highest adsorption selectivity for CO_2 over N_2 in the whole pressure range.
- The competitive adsorption between CO_2 and water molecules was studied for IL@CNTs composites.

GRAPHICAL ABSTRACT

Carbon nanotube bundles supported with room-temperature ionic liquids for selective separation of CO_2/N_2 under the presence of water.



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ABSTRACT

Novel gas adsorption properties by room-temperature ionic liquids (ILs) confined in carbon nanotube (CNT) bundles were ascertained using grand canonical ensemble Monte Carlo (GCMC) simulations in which the adsorption and separation of CO_2 from CO_2/N_2 mixtures. The introduction of ILs into the CNT channels significantly enhances the adsorption of CO_2, while it is not sensitive to N_2 adsorption. This is due to the strong interaction between specific ILs in the CNTs and CO_2 molecules. The presence of water showed a significant impact on the adsorption capacity of CO_2 as well.

1. Introduction

The capture and separation of CO_2 from a gas mixture in power plants is very important, because it is the major greenhouse gas contributor to the climate change (Dawson et al., 2011; Nugent et al., 2013). An increase of CO_2 concentration in the atmosphere has been observed from around 280 ppm to 390 ppm over the last few decades (Rochelle, 2009; Hoeven, 2011). The capture and separation of CO_2 from gas mixtures require urgent actions, and hence is of great interest in both academic and industrial perspectives.

Techniques have been proposed for CO_2 capture and separation, such as adsorption, cryogenic distillation, membrane permeation and amine scrubbing (Bae et al., 2013; Joos et al., 2015; Shen et al., 2015). In the scope of adsorption, room-temperature ionic liquids (rILs) are recognized as environmentally-friendly adsorbents for CO_2 capture (Plechkova and Seddon, 2008; Shiflett et al., 2010), and their adsorption performance can be tuned by changing the combination of constituting anions/cations

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* Corresponding author.
E-mail address: ypzeng@yzu.edu.cn (Y. Zeng).

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(Anantharaj and Banerjee, 2013; Shi and Maginn, 2008b). The behavior of CO_2 interacting with different types of rILs has been studied by the experimental and theoretical techniques (Bates et al., 2002; Blanchard et al., 1999; Blath et al., 2011; Gonzalez-Miquel et al., 2011; Karadas et al., 2010; Lei et al., 2013; Liu et al., 2003; Muldoon et al., 2007; Sánchez Fuentes et al., 2017; Shi and Maginn, 2008a; Shiflett and Yokozeki, 2005; Sistla et al., 2012; Wang et al., 2011a). ILs exhibit reduced energy consumption and high adsorption capacities in general (Anantharaj and Banerjee, 2013; Shiflett et al., 2010). ILs was seldom directly used, due to the high viscosity and small gas-liquid interfaces resulting in low absorption/desorption rates and high amount required (Gutowski and Maginn, 2008). Alternatively, ILs impregnated in porous materials have been proposed to mitigate the drawbacks mentioned above as well as to enhance the mechanical strength and to reduce the mass transport limitation (Lemus et al., 2011; Lozano et al., 2011; Scovazzo, 2010).

A couple of studies exploring the excellence of CO_2 capture and separation were reported using ILs supported on polymeric materials, e.g., nonhexafluorophosphate ionic liquid on polyethersulfone (Scovazzo et al., 2004), amine-functionalized ionic liquid on the nylon support (Myers et al., 2008), and 1-n-alkyl-3-methylimidazolium-based ionic liquids on polyvinylidene fluoride (Neves et al., 2010). In addition, metal-organic frameworks (MOFs), exhibiting versatile properties of large pore volume, high surface areas and tailorable structures (Babarao and Jiang, 2009; Düren et al., 2009; Wilmer et al., 2012; Yang et al., 2013; Chung et al., 2016; Flaig et al., 2017), was studied as supports for ILs for CO_2 capture and separation from CO_2/N_2 mixtures, such as [Bmim][PF_6] (1-Butyl-3-methylimidazolium hexafluorophosphate) on IRMOF-1(Chen et al., 2011) and ILs on Cu-BTC (Chen et al., 2011). It was found that the anion type and loading of ionic liquids has influential effect on the separation performance (Vicent-Luna et al., 2013), and the [Bmim][SCN](1-Butyl-3-methylimidazolium thiocyanate)/MOF membranes showed even higher CO_2 selectivity and permeability in comparison with many other polymer membranes (Gupta et al., 2013). In addition, high surface nanoporous carbons prepared from imidazolium-based ionic liquid/MIL-100 composites were shown a high CO_2 uptake capacity and selectivity (Aijaz et al., 2014).

However, for CO_2 capture, especially in post-combustion processes, adsorbents are required to exhibit strong stability under higher temperature, sever acid and moisture conditions. Unfortunately, the majority of organic polymers will lose the stability under the high temperature and most MOFs are likewise unstable in aqueous solutions (De Toni et al., 2012; Greathouse and Allendorf, 2006; Huang et al., 2003; Schoenecker et al., 2012). CNTs were found to capture CO_2 nearly twice as much as activated carbons (ACs) at the temperature of 0–200 °C (Cinke et al., 2003), and exhibited a higher selectivity for CO_2 in CO_2/CH_4 mixtures compared to some zeolites 13X, activated carbons and MOFs (Huang et al., 2007). As known, carbon nanotubes (CNTs) possess nanosize hollow tubes with good stability under severe conditions, and have been studied for gas storage applications (Chen et al., 1999; Dillon et al., 1997; Ma et al., 2001). CNTs can also encapsulate many organic/inorganic solvent and inorganic ions (Tasis et al., 2006). ILs can also be encapsulated stably by the confinement effect in CNTs where the crystal formation of ILs, e.g., [Bmim][PF_6] can be clearly observed (Chen et al., 2007; Dong et al., 2009). Considering the unique advantages of ILs and CNTs, the combination of CNTs and rILs could be attractive adsorbents for CO_2 capture and separation from gas mixtures. This work explores the rILs/CNTs composite as a suitable candidate for the capture and separation of post-combustion CO_2. It would give a better insight of adsorption properties of IL@CNTs for post-combustion mixture.

2. Computational methods

2.1. Models and force field

CNTs were reported to form bundles with different nanotube numbers (Journet et al., 1997). The open-ended CNT bundles exhibit two types of energetically favorable adsorption sites, namely the inner and the interstitial regions (Jiang and Sandler, 2004). The inner regions provide an opportunity for ionic liquids to enter.

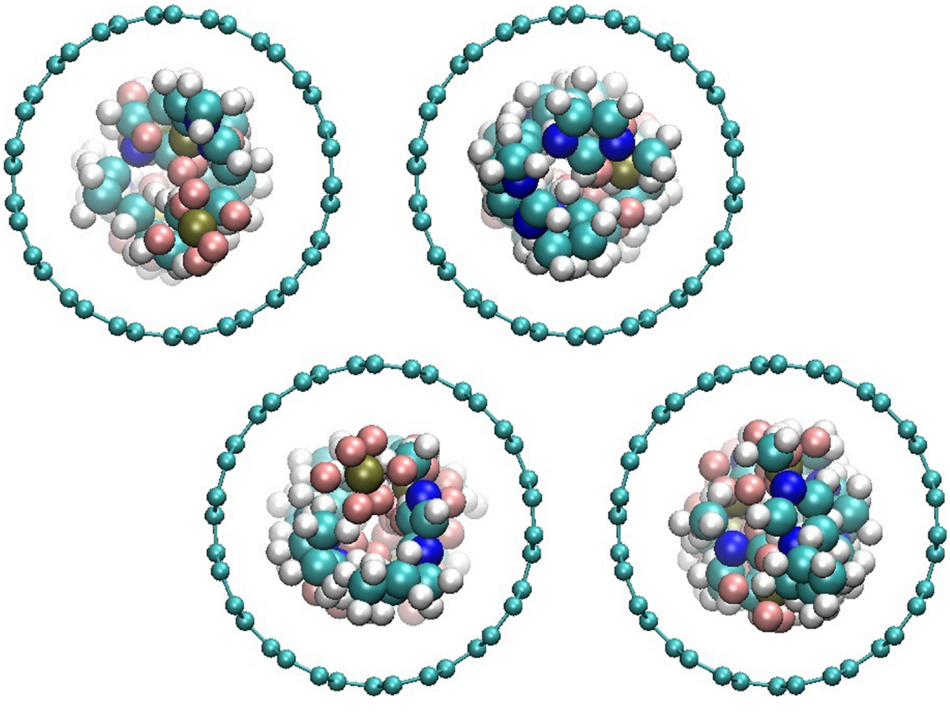

Fig. 1. Periodic nanotube bundles supported with ionic liquid.