



Low-viscous fluorine-substituted phenolic ionic liquids with high performance for capture of CO₂

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HIGHLIGHTS

- The viscosities of the phenolic ionic liquids are less than 64.8 cP at 303.2 K.
- The absorption equilibrium times are within 230 s at 313.2 K.
- The CO₂-absorption molar ratio of [P₄₄₄₄][4-F-PhO] is as high as 0.842.
- The ILs could be carried out with no obvious loss in the absorption of CO₂.

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ABSTRACT

Three fluorine-substituted phenolic ionic liquids, namely tetrabutylphosphonium 2-fluorophenolate ([P₄₄₄₄][2-F-PhO]), tetrabutylphosphonium 3-fluorophenolate ([P₄₄₄₄][3-F-PhO]), and tetrabutylphosphonium 4-fluorophenolate ([P₄₄₄₄][4-F-PhO]), were synthesized in this work. The ionic liquids prepared were characterized by ¹H NMR, ¹³C NMR, FT-IR, and ESI-MS spectroscopies and their physical properties including densities, viscosities and decomposition temperatures were also determined. The viscosities of the three fluorine-substituted phenolic ionic liquids are not more found to be less than 64.8 cP at 303.2 K. As a result, the rate of CO₂ absorption is very fast and the absorption equilibrium time is within 230 s at 313.2 K. The CO₂-absorption capacity of [P₄₄₄₄][2-F-PhO], [P₄₄₄₄][3-F-PhO], [P₄₄₄₄][4-F-PhO] at 1.0 bar and 313.2 K are as high as 0.673, 0.741, 0.842 in molar ratio, respectively. Furthermore, the ionic liquids were carried out for five cycles with no obvious loss in the absorption capacity of CO₂. Quantum chemical calculations and spectrum study are also used to investigate the interaction between phenolic ionic liquids and CO₂ molecules.

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1. Introduction

The emission of greenhouse gas (e.g., CO₂) which results in global warming is a widely concerned environmental issue throughout international communities. To address this issue, a growing number of researches have been performed in the field of CO₂ capture over the last decades. Volatile aqueous organic amines [1] are usually used for the capture of CO₂ in traditional processes. However, there are many disadvantages, such as volatility, decomposition, corrosion and high energy consumption. Therefore, exploring green solvents to replace traditional organic amines for the capture of CO₂ is rather desired. To this purpose, ionic liquids are good candidates.

Ionic liquids (ILs) are a type of organic molten salts. They have various unique properties including wide liquid temperature range, extremely low vapor pressure, high thermal stability, designable structure and good solubilization for many compounds [2–4], especially acidic gases [5]. As a result, ILs have great potential application in such fields as electrolytes [6], solvents [7], catalysis [3,4,8], gas separation [9–14], etc. Especially for the design of energy-efficient liquid absorbents for CO₂ capture, ILs show significant superiority to other volatile organic solvents.

Davis et al. [15] reported the first amine-functionalized ionic liquid for the absorption of CO₂. It could trap CO₂ with a stoichiometric of 0.5 mol CO₂/mol IL through the formation of ammonium carbamate. Subsequently, numerous studies reported a variety of amine-functionalized ionic liquids for the capture of CO₂. For instance, Zhang et al. [16] synthesized a series of phosphonium-based amino acid ionic liquids and they were supported on porous silica gel for the absorption of CO₂ with enhanced kinetics. The

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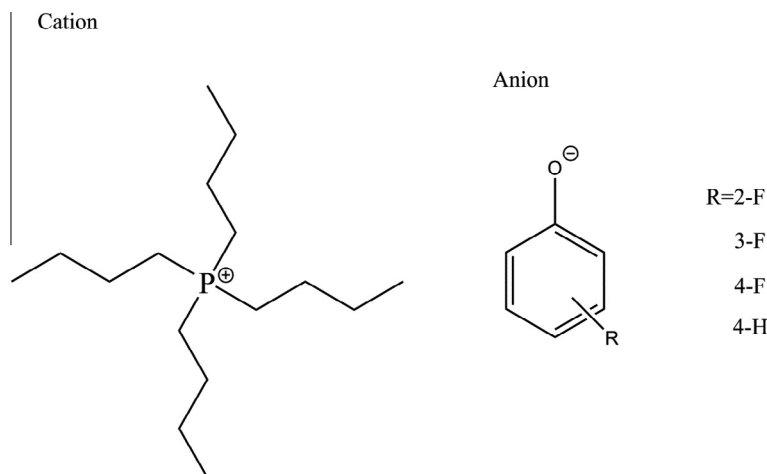


Fig. 1. Structures of the cation and the anions in phenolic ionic liquids.

same group further designed a series of dual amine-functionalized phosphonium-based and imidazolium-based ionic liquids [17,18]. The molar ratio absorption capacity of CO_2 could approach 1 mol CO_2 /mol IL. Dai et al. [19] synthesized diverse phenolic ionic liquids with the substituent on the anion, but results showed high viscosities so that it was unfavorable for the uptake of CO_2 . Our group also designed a class of low-viscous tetraalkylammonium amino acid ILs with high rate for the absorption CO_2 . However, the viscosity of amino acid ILs would increase drastically during the absorption of CO_2 due to the formation of complex network of hydrogen bonds. Therefore, ILs containing aprotic heterocyclic anions (AHAs) with strong basicity (e.g., azole-based ILs, pyrrolidine-based ILs, phenolic ILs, etc.) were introduced by Brennecke et al. [20] and Wang et al. [21,22] for the equimolar capture of CO_2 . Due to the absence of complex network of hydrogen bonds, the viscosity of AHAs-based ILs would change only slightly after saturated with CO_2 . Among AHAs-based ILs, phenolic ILs are a class of promising ILs because their physicochemical properties could be easily tuned by grafting various electron-withdrawing or electron-donating groups to the benzene ring.

However, the viscosities of the ionic liquids reported in literature are still relatively high [19,23–27]. This would interfere the real application of ionic liquid because great energy would be required to transport liquids with such high viscosity. In order to address this problem, we designed three new fluorine-substituted phenolic ILs with low viscosity: tetrabutylphosphonium 2-fluorophenolate ($[\text{P}_{4444}][2\text{-F-PhO}]$), tetrabutylphosphonium 3-fluorophenolate ($[\text{P}_{4444}][3\text{-F-PhO}]$) and tetrabutylphosphonium 4-fluorophenolate ($[\text{P}_{4444}][4\text{-F-PhO}]$). They were found to exhibit much lower viscosities than other phenolic ILs. We investigated their performance for the capture of CO_2 systematically in this work.

2. Experimental

2.1. Materials

Carbon dioxide was supplied from Nanjing Weichuang Gas Co., Ltd. (China) with a minimum purity of 99.99 mol%. Phenol (AR grade, 99 wt%) and silver oxide (AR grade, 99.5 wt%) were both purchased from Sinopharm Chemical Reagent Co., Ltd. 2-Fluorophenol (AR grade, 98 wt%), 3-fluorophenol (AR grade, 98 wt%), 4-fluorophenol (AR grade, 99 wt%) were all purchased from Adamas Reagent Co., Ltd. Tetrabutylphosphonium bromide (AR grade, 98 wt%) was purchased from Energy Chemical Co., Ltd.

2.2. Preparation and characterization of ILs

The three fluorine-substituted phenolic ILs investigated in this work were tetrabutylphosphonium 2-fluorophenolate ($[\text{P}_{4444}][2\text{-F-PhO}]$), tetrabutylphosphonium 3-fluorophenolate ($[\text{P}_{4444}][3\text{-F-PhO}]$) and tetrabutylphosphonium 4-fluorophenolate ($[\text{P}_{4444}][4\text{-F-PhO}]$). For comparison, a nonfluoro-substituted ILs tetrabutylphosphonium phenolate ($[\text{P}_{4444}][\text{PhO}]$) was also synthesized. Their chemical structures were illustrated in Fig. 1. All of them were prepared through a two-step procedure. Taking tetrabutylphosphonium 2-fluorophenolate ($[\text{P}_{4444}][2\text{-F-PhO}]$) as an example, in the first step, tetrabutylphosphonium bromide ($[\text{P}_{4444}][\text{Br}]$) was dissolved in 100 ml of ethanol and loaded into a 250 ml flask with a magnetic stirrer. Then stoichiometric silver oxide was slowly added within 2 h and the reaction lasted for 24 h under dark condition. Resulted silver bromide was separated by filtration to offer ethanol solution of tetrabutylphosphonium hydroxide ($[\text{P}_{4444}][\text{OH}]$). In the second step, equimolar 2-fluorophenol dissolved in 50 ml of ethanol was added dropwise to the ethanol solution of $[\text{P}_{4444}][\text{OH}]$ within 2 h. The neutralization reaction lasted for 12 h in ice bath. After completion, solvents were removed by evaporation under reduced pressure. The resulting liquid was dried under vacuum at 80 °C for at least 48 h and a black product was obtained. The synthesis procedure for $[\text{P}_{4444}][\text{PhO}]$,

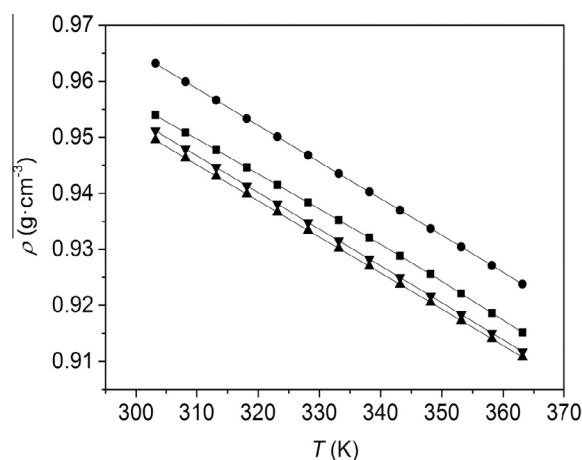


Fig. 2. Densities of phenolic ionic liquids as a function of temperature (■ $[\text{P}_{4444}][\text{PhO}]$; ● $[\text{P}_{4444}][2\text{-F-PhO}]$; ▲ $[\text{P}_{4444}][3\text{-F-PhO}]$; ▼ $[\text{P}_{4444}][4\text{-F-PhO}]$).

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