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A novel hydrophilic amino acid ionic liquid [C_2OHmim][Gly] as aqueous sorbent for CO_2 capture

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ABSTRACT

Since functionalized ionic liquid (ILs) could achieve excellent performance on CO_2 capture by introducing suitable moieties in the conventional ionic liquids, design and synthesis of new ionic liquids have been attracting remarkable interests. In this work, we designed a novel hydrophilic amino acid ionic liquid ([C_2OHmim][Gly]) that was functionalized based on the imidazolium ionic liquid with glycine anions and hydroxy group for CO_2 absorption. The absorption capacity of [C_2OHmim][Gly] was 0.575 mol CO_2/mol absorbent that was similar to the equimolar stoichiometry following the zwitterion mechanism. Simple synthesis, large absorption capacity, good resistance to O_2, and high regeneration efficiency make this functionalized ILs great potential for making up the deficiencies of aqueous MEA, therefore benefiting industrial applications.

1. Introduction

As one of the most important greenhouse gases, treatment of CO_2 has attracted more attention. Carbon capture technologies have been greatly developed in recent years (Markewitz et al., 2012; IPCC, 2005); especially in primary power stations and industries that burn fossil fuels. For post combustion CO_2 capture process, amine solvents, 30 wt% monoethanolamine (MEA), appear to be a viable option and are the most widely used examples (MacDowell et al., 2010; Luo et al., 2015). However, the utilization of these solvents still suffers several shortcomings, such as equipment corrosion, easy heat decomposition, oxidation of amines, and secondary pollution, due to its high volatility (Barbarossa et al., 2013; MacKenzie et al., 2007; Leonard et al., 2015; Luo et al., 2015; Yeh et al., 2005).

To overcome these issues, many economical solvents were desired to capture CO_2 (Conway et al., 2015; Liang et al., 2015). Amino acid salt (AAS) is one of the alternative solvents for CO_2 capture. Many of them are naturally existed and have no environmental or toxic issue (Aronu et al., 2010). Hence, they are easily obtained, biocompatible and biodegradable (Xue et al., 2011). Meanwhile, CO_2 absorption capacity of amino acid salts is comparable to that of aqueous alkanolamines and has better resistance to degradation (Chang et al., 2015). However, the most potential drawback of amino acid salt solutions is possible precipitation during CO_2 absorption (Majchrowicz et al., 2009), resulting in a decreased CO_2 absorption capacity after multiple regeneration.

In recent years, ionic liquids (ILs) are considering to be green solvents due to their negligible volatility and remarkable thermal stability (Jiang et al., 2008). However, gas dissolution into room-temperature ILs is a physical phenomenon with no chemical reaction and the absorption rate is quite slow. In order to achieve better performance, some special groups were introduced to the anion or the cation of ILs. There are many kinds of functionalized ILs, especially functional ILs with the amino group. They are synthesized to achieve excellent performance in CO_2 capture due to the following characteristics: low volatility, low heat required for reaction, low thermal and oxidative degradation, and high absorption capacity and easy to be regenerated (McDonald et al., 2014; Yang and He, 2014; Zhang et al., 2013b).

A new functionalized ILs with amino acid based (AAILs) has aroused considerable interests, which have the advantages of ionic liquids and amino acid salt at the same time and aim to overcoming the defects of each single absorbent. In 2005, [emim][amino acid] was synthesized for CO_2 absorption (Fukumoto et al., 2005). Then a series of tetraalkylammonium-based amino acid ILs were successfully synthesized and could rapidly absorb CO_2 (Guo et al., 2013, 2015; Ma et al., 2011; Zhang et al., 2013a). It was found that an absorption capacity of 2.1 mol CO_2/mol IL (3.5 mol CO_2/kg IL, 13.1 wt% CO_2) for [N_{66614}][Lys] at ambient temperature and about

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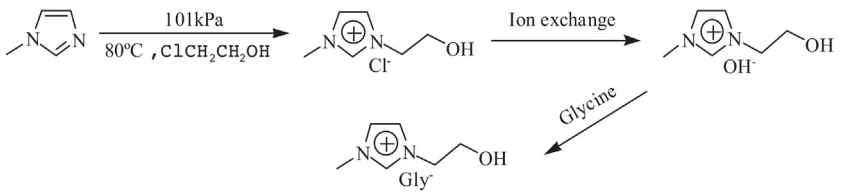

Fig. 1. Synthesis schematics of [C_2OHmim][Gly].

1 mol CO_2/mol IL at 80 °C (under 1 bar of CO_2), which was higher than MEA solution. AAILs seem to be a promising absorbent for CO_2 capture.

Our group was also devoted to designing an effective absorbent for CO_2 capture in recent years (Lu et al., 2013). Herein, a AAILs based on the imidazolium cation that contains additional functional anions with glycine was synthesized. Furthermore, a hydroxy group was introduced to these AAILs in order to improve the hydrophilicity of the AAILs in aqueous solution and to facilitate the process for CO_2 absorption.

2. Materials and methods

2.1. Chemicals

1-Methylimidazole (≥99.0%), glycinate (≥99.0%) and 2-Chloroethanol (≥99.0%) was purchased from Chengdu Xi Ya Chemical Reagent Co. Ltd, China. Sodium glycinate (H_2NCH_2COONa) (analytical grade) was provided by Su Zhou Yong Da Chemical Reagent Co. Ltd, China. CO_2 (>99.99%), O_2 (>99.99%) and N_2 (>99.99%) were provided by Zhejiang Jin-gong Gas Co, China. All the other chemicals were analytical grade and commercially available without further purification.

2.2. Synthesis of the functionalized ILs

The amino acid ionic liquid [C_2OHmim][Gly] was synthesized in the laboratory by replacement reaction. The synthesis reaction was divided into two steps. Synthesis of [C_2OHmim][Gly] was shown in Fig. 1. Firstly, Chlorinated-1-hydroxyethyl-3-methylimidazolium ([C_2OHmim]Cl) was synthesized by the reaction of 1-Methylimidazole and 2-Chloroethanol. 2-Chloroethanol (0.6 mol) was gradually dripped into a three-necked flask filled with 1-Methylimidazole (0.5 mol). The reaction was carried out for 24 h at 80 °C under continuous stirring. The resulting product was evaporated at 70 °C to eliminate unreacted raw material and cooled for crystallization of product. The crystallization was purified by extraction using ethyl acetate to remove the raw material. At last, the product was put into a vacuum oven and dried for 48 h to get [C_2OHmim]Cl. In the second step, [C_2OHmim][Gly] was synthesized by the reaction of [C_2OHmim]Cl and sodium hydroxide via ion exchange, followed by neutralization reaction with glycinate (Zhang et al., 2010a,b). [C_2OHmim]Cl (0.1 mol) and sodium hydroxide (0.10 mol) were added into the three-necked flask. The reaction was carried out for 12 h at 0 °C under stirring. The unreacted sodium hydroxide was then filtered when the product was washed by Methanol and Ethyl acetate. The product was evaporated by rotary evaporation and purified. [C_2OHmim][Gly] was seen to be liquid at room temperature and would be crystallized when temperature reduced.

2.3. Characterization

The thermal characterization of [C_2OHmim][Gly] was analyzed with Thermo gravimetric analyzer (SDT Q600) by heating samples from 30 °C to 700 °C with a heating rate of 10 °C min^{-1} in N_2 atmosphere.

The infrared spectra of [C_2OHmim][Cl] and [C_2OHmim][Gly] were obtained between 400 cm^{-1} and 4000 cm^{-1} using Fourier Trans-form Infrared Instrument (Nicolet iS50).

The samples of [C_2OHmim][Gly] before and after reaction with CO_2 were characterized by ^{13}C NMR (Agilent 600 MHz DD2), using D_2O as solvent.

2.4. Experimental procedure

The absorption experiments were carried out in a double stirred-cell absorber that was also used in our previous work (Lu et al., 2013) and a schematic diagram of the experimental setup was shown in Fig. 2(a). CO_2 and O_2 gas were mixed with N_2 to simulate the typical flue gas. The total gas flow rate was adjusted to 0.5 L min^{-1} by using a mass flow controller. The experiments in this work were investigated in aqueous solution with a low CO_2 partial pressure (10 kPa), which was in accordance with actual situation. The functional IL was dissolved in the water to form a mixed solution for CO_2 capture. CO_2 absorption capacity, which was defined as moles of CO_2 absorb/mole of absorbent, was investigated using a double stirred-cell at 305.15 K with a molar concentration of absorbent as 0.4 mol L^{-1}. The weight percentage of the functional IL was approached 8%. The absorption volume was 250 ml. A series of experiments were carried out under different concentrations. The

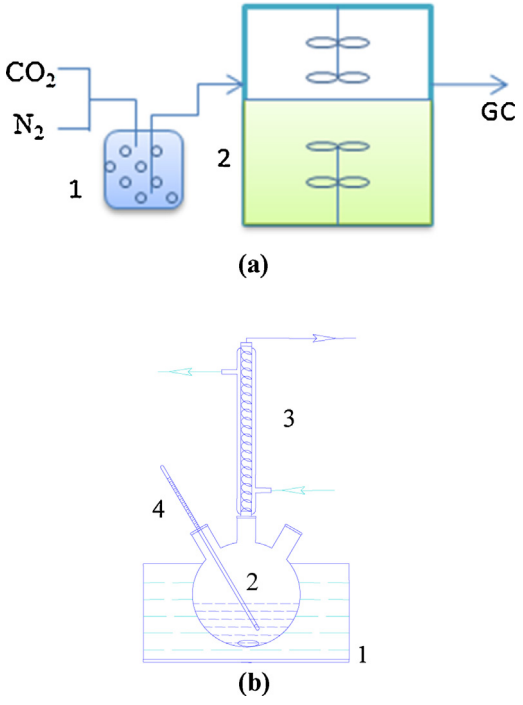

Fig. 2. (a) Schematic diagram for CO_2 capture. 1 – Gas mixer; 2 – stirred-cell absorber. (b) Schematic diagram for CO_2 desorption. 1 – Magnetic stirring apparatus with oil bath; 2 – flask; 3 – condenser tube; 4 – thermometer.