



# Low-viscous diamino protic ionic liquids with fluorine-substituted phenolic anions for improving CO<sub>2</sub> reversible capture

Tianxiang Zhao, Xiaomin Zhang, Zhuoheng Tu, Youting Wu\*, Xingbang Hu\*

School of Chemistry and Chemical Engineering, Separation Engineering Research Center, Key Laboratory of Mesoscopic Chemistry of MOE, Nanjing University, Nanjing 210093, PR China

## ARTICLE INFO

### Article history:

Received 4 July 2018

Received in revised form 18 July 2018

Accepted 23 July 2018

Available online 24 July 2018

### Keywords:

CO<sub>2</sub> capture

Ionic liquids

Fluorine-substituted phenolic

DMAPA

## ABSTRACT

Ionic liquids (ILs) have been widely investigated as the promising green absorbents for CO<sub>2</sub> capture. In this work, four low-viscous diamino protic ionic liquids (PILs), including *N,N*-dimethyl-1,3-propane diamine 2-fluorophenolate ([DMAPAH][2F-PhO]), *N,N*-dimethyl-1,3-propane diamine 3-fluorophenolate ([DMAPAH][3F-PhO]), *N,N*-dimethyl-1,3-propane diamine 3-fluorophenolate ([DMAPAH][4F-PhO]), and *N,N*-dimethyl-1,3-propane diamine 3,5-difluorophenolate ([DMAPAH][3,5F-PhO]), were prepared and evaluated for CO<sub>2</sub> capture. The solubilities of CO<sub>2</sub> in these PILs were measured using an isochoric saturation technique at temperatures from 303.2 to 333.2 K and pressure up to 1.5 bar. It was found that the PILs are excellent absorbent for CO<sub>2</sub> capture with the best absorptive capacity of 3.99 mol CO<sub>2</sub>/kg IL (0.86 mol CO<sub>2</sub>/mol IL), which is superior or competitive to most reported ILs. Furthermore, the captured CO<sub>2</sub> was easy to release by heating and decompression, leading regeneration of the PILs. In addition, a plausible mechanism of CO<sub>2</sub> absorption in these PILs was proposed via a combination of chemical and physical absorption by NMR, FTIR, and mass spectrum (MS).

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## 1. Introduction

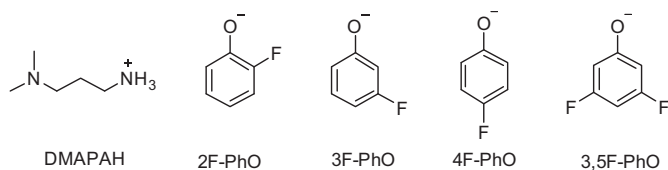
Currently, aqueous organic amines are the cost-effective absorbents for acidic gas capture in industrial processes such as CO<sub>2</sub> emission of coal-fired power plants. The techniques have been used widely in the chemical industry for many years. However, amines employed in these processes exhibit multiple drawbacks such as corrosiveness, volatility, occasional decomposition, and high energy cost for regeneration [1, 2]. Notably, how to reduce the volatilization loss of amine in the process of CO<sub>2</sub> capture by organic amine has become one of the main research focuses. In this respect, Jeessop and co-workers [3–5] reported an innovative class of CO<sub>2</sub> binding organic liquids (CO<sub>2</sub>BOLs) consisted of alcohol and guanidine (or amidine) superbase. These systems are based on the formation of liquid guanidinium or amidinium alkylcarbonate salts exhibiting remarkable activity as switchable surfactants. However, they failed to attract industrial attention for CO<sub>2</sub> capture possibly due to the high cost involved in the utilization of guanidine or amidine. Inspired by the classic alkanolamine for CO<sub>2</sub> capture, we demonstrated recently the tandem systems of 1,2-ethanediamine and a series of ethylene glycol derivatives that bound CO<sub>2</sub> to form solid CO<sub>2</sub> storage material (CO<sub>2</sub>SM) [6, 7]. Due to the excellent water stability of CO<sub>2</sub>SM, it has been shown to have potential application as fast-acting fertilizer for enhanced plant growth. Although above the systems demonstrated obvious advantages in terms

of price, the weight-uptake of CO<sub>2</sub> was still low. To this end, we input sequentially a lot of attention and interest in developing of efficient and reversible materials for removal of CO<sub>2</sub>.

Ionic liquids (ILs), one of the most promising alternatives for removal of CO<sub>2</sub>, have received much attention in the field of CO<sub>2</sub> separation due to their unique features such as high thermal stability, negligible vapor pressure, and adjustable chemical properties [8, 9]. In fact, the exorbitant price and high viscosity of ILs restrict their practical applications in industrial processes. Protic ionic liquids (PILs), as a class of cost-effective ILs, may be able to bypass the problems of classical ILs [10, 11]. Usually, PILs can be easily prepared from simple materials through the transfer of a proton from a Brønsted acid to a Brønsted base, in which the volatility of Brønsted base such as amine can be restrained significantly. Indeed, many amine-based PILs, paired with carboxylic acids [12], phenol derivatives [13], and imidazole derivatives [14], have been used for removal of CO<sub>2</sub> or SO<sub>2</sub>. For example, the typical superbase-based PILs with low melting points were developed by Wang [15], which were capable of reversibly capturing CO<sub>2</sub> with an extremely high capacity of up to 1 mol CO<sub>2</sub>/mol IL. However, since these superbases were heavy, resulting in high-viscous PILs, meanwhile, the high price of the starting material could be expected to limit its applicability. Subsequently, Vijayraghavan et al. [16] synthesized a series of diamine carboxylate PILs, giving an absorptive capacity of 0.33 mol CO<sub>2</sub>/mol IL (2.03 mol CO<sub>2</sub>/kg IL). Notably, the lower basicity of the amine sites decreased the binding energy of the CO<sub>2</sub> to the PILs, resulting in a significant reduction in energy required to strip absorbed CO<sub>2</sub> [16]. Recently, Oncsik etc. [17] demonstrated a novel strategy for

\* Corresponding author.

E-mail addresses: [ytwu@nju.edu.cn](mailto:ytwu@nju.edu.cn) (Y. Wu), [huxb@nju.edu.cn](mailto:huxb@nju.edu.cn) (X. Hu).



**Fig. 1.** The Chemical structures of cations and anions for the four investigative diamino PILs.

removal of CO<sub>2</sub> by *N,N*-dimethyl-1,3-propane diamine (DMAPA)-based PILs using azolide anions. These PILs rapidly absorbed CO<sub>2</sub> to >5 mol CO<sub>2</sub>/kg IL pointing towards equimolar absorption, suggesting that DMAPA was an excellent alternative for the preparation of PILs with high CO<sub>2</sub> absorption capacity. In the course of our study on the capture of CO<sub>2</sub>, we discovered that the low-viscous fluorine-substituted phenolic ILs revealed appreciable and reversible performance for CO<sub>2</sub> capture along with the best absorptive capacity of 0.84 mol CO<sub>2</sub>/mol IL [18]. Inspiring by above researches, the diamino PILs were designed firstly by DMAPA and fluorophenol for the removal of CO<sub>2</sub>. These low viscosity diamino PILs were capable of reversibly capturing CO<sub>2</sub> with an extremely high capacity of ~3.99 mol CO<sub>2</sub>/kg IL (0.86 mol CO<sub>2</sub>/mol IL). Furthermore, the absorption mechanism was also researched by NMR, FTIR, mass spectrum (MS). Particularly, the interaction of F<sup>-</sup> ··· CO<sub>2</sub>, lacking in known fluoride-containing ILs, was furtherly discussed in this work. The results will be of great relevance for the development of the practical and efficient capture medium of CO<sub>2</sub>.

## 2. Experimental section

### 2.1. Materials and instrument

*N,N*-dimethyl-1,3-propane diamine (DMAPA), 2-fluorophenol (2F-PhOH), 3-fluorophenol (3F-PhOH), 4-fluorophenol (4F-PhOH), and 3,5-difluorophenol (3,5F-PhOH) were purchased from Adamas Chemical Co., Ltd. All reagents were obtained in the highest purity grade (>99 wt%) and directly used as received without further purification unless otherwise indicated. CO<sub>2</sub> and N<sub>2</sub> (99.99 wt.%), supplied by Nanjing Messer Gas, Nanjing University (China), were employed to determine the CO<sub>2</sub> absorptive capacity of PILs. The Bruker AV 400 spectrometer was used to conduct the NMR experiments. FTIR spectra were recorded on a Nicolet iS50 infrared spectrometer. Elemental analysis (EA) was taken by an Elementar vario EL II. The Electrospray mass spectrometry (ESI-MS) were determined with a LCQ-fleet ESI mass spectrometer. The Shimadzu GC-2014 gas chromatograph with a flame-ionization detector was employed for analyzing mechanism of CO<sub>2</sub> absorption.

### 2.2. Synthesis and characterization of PILs

Typically, the 15 mL of ethanol solution of 4F-PhOH (20 mmol) was added drop wisely to the 15 mL of ethanol solution of DMAPA (20 mmol). The reaction was stirred for 2 h in ice bath and the mixture was warmed to 50 °C and stirred for 8 h. After that, the ethanol was removed by evaporation under reduced pressure. The resulting crude

product was washed for three times with dimethyl ether to remove unreacted reactants. The obtained product was dried under vacuum at 50 °C for 24 h to remove trace of solvent to offer a brownish liquid [DMAPAH][4F-PhO]. The chemical structures of the prepared PILs in this work were confirmed by NMR spectra, ESI-MS, EA, and FTIR spectra.

### 2.3. Physical properties of PILs

The density and viscosity of these PILs were measured in the temperature range of (298.2 to 333.2) K. The densities were determined using a DM40/DM45 DeltaRange/DM50 automatic densimeter with a precision of 0.0001 g · cm<sup>-3</sup>, which was calibrated using distilled water. Viscosities were measured on a HAAKE Rheostress 600 viscometer with an uncertainty of ±1% in relation to the full scale. The measurement temperatures were controlled by a bath with an uncertainty of ±0.1 K. TG traces were recorded on a PerkinElmer Pyris 1 TGA from room temperature to 400 °C with a scanning rate of 10 °C · min<sup>-1</sup> under N<sub>2</sub> atmosphere to determine the decomposition temperatures of ILs.

### 2.4. Absorption and desorption of CO<sub>2</sub>

Solubility of CO<sub>2</sub> in four PILs were measured by isothermal gas-liquid equilibrium experiments at temperatures from 303.2 to 333.2 K and pressure up to 1.5 bar. The experimental instrument and process, treating data, and error analysis were identical to our previous works [19, 20]. The measuring temperature was kept constant by a circulation water bath with an uncertainty of ±0.1 K. The pressure was determined by a pressure gauge with an accuracy of ±0.006 bar. Duplicate experiments were run for each absorbent to obtain averaged values of CO<sub>2</sub> absorption. The averaged relative deviations of the absorption data are well within ±3% in this work. The absorptive capacities of CO<sub>2</sub> both in the unit of molality (mol CO<sub>2</sub>/kg IL) and molar ratio (mol CO<sub>2</sub>/mol IL) were introduced to evaluate the absolute and relative CO<sub>2</sub> uptake. To inspect the recyclability of PILs, the CO<sub>2</sub>-saturated IL was heated to 353.2 K under a pressure of 10 kPa for 1 h and then reused for the determination of CO<sub>2</sub> solubility.

## 3. Results and discussion

### 3.1. Characterization of ILs

The investigated diamino PILs in this work, including [DMAPAH][2F-PhO], [DMAPAH][3F-PhO], [DMAPAH][4F-PhO], and [DMAPAH][3,5F-PhO], were prepared by direct neutralization between DMAPA and desired fluoro-substitution phenol. Their chemical structures are shown in Fig. 1. The NMR and ESI-MS showed the formation of the PILs, indicating that the proton on fluoro-substitution phenol was completely transferred to the amine in each case. The NMR, EA, FTIR and ESI-MS spectra were found to be in good agreement with their corresponding chemical structures. No impurities were found according to characterization results.

[DMAPAH][2F-PhO]: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.02–6.85 (m, 3H), 6.69 (d, *J* = 7.8 Hz, 1H), 5.67 (s, 3H), 2.78 (t, *J* = 6.9 Hz, 2H), 2.40–2.35 (m, 2H), 2.24 (s, 6H), 1.72–1.61 (m, 2H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 153.61, 151.23, 146.33, 124.56, 118.86, 118.51, 115.74, 57.45, 45.11, 40.26, 29.56 ppm. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>)

**Table 1**  
Densities and viscosities of the investigative PILs at temperature range of (293.2 to 333.2) K.

ILs & temperature (K)	298.2	303.2	313.2	323.2	333.2	298.2	303.2	313.2	323.2	333.2
	Density (g · cm <sup>-3</sup> )					Viscosity (cP)				
[DMAPAH][2F-PhO]	1.0671	1.0623	1.0397	1.1281	1.0671	284.1	154.7	55.7	24.5	12.6
[DMAPAH][3F-PhO]	1.0619	1.0576	1.0350	1.1232	1.0619	77.2	50.8	25.5	12.4	6.8
[DMAPAH][4F-PhO]	1.0514	1.0477	1.0252	1.113	1.0514	38.7	27.4	13.8	7.1	4.1
[DMAPAH][3,5F-PhO]	1.0407	1.0378	1.0151	1.1028	1.0407	147.1	88.4	38.5	18.5	9.4

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