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CO_2 absorption behavior of azole-based protic ionic liquids: Influence of the alkalinity and physicochemical properties

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ABSTRACT

Recently, chemical fixation of CO_2 catalyzed by protic ionic liquids (PILs) has been successfully achieved, suggesting that CO_2 absorption behavior plays an important role on CO_2 activation and transformation. For this reason, the influence of the alkalinity and physicochemical properties on CO_2 absorption behavior of four azole-based PILs, namely [DBNH][Pyr], [DBNH][Im], [DBUH][Pyr], and [DBUH][Im] was discussed in this work. The alkalinity of PILs was determined by potentiometric titration, and free space of PILs was evaluated by thermal expansion coefficient and refractive index. Solubility parameter of PILs was obtained from the activation energy for viscous flow. The results show that PILs with $[Pyr]^-$ exhibits stronger alkalinity and larger free space, which can help to improve CO_2 capture capacity. Whereas PILs with larger cation size $[DBUH]^+$ exerts higher viscosity, resulting in slower absorption rate of CO_2. Furthermore, the CO_2 absorption capacity is inversely proportional to the solubility parameter of PILs. The absorption mechanism proved by FT-IR and ^{13}C NMR spectra indicates that $[Pyr]^-$ or $[Im]^-$ can react with CO_2 to form carbamate. Accordingly, considering the CO_2 capture capacity and absorption rate, [DBNH][Pyr] may be a good candidate for efficient CO_2 capture and activation with low enthalpy of absorption of $-38.2\ kJ\ mol^{-1}$.

1. Introduction

The concentration of CO_2 in the atmosphere is at their highest recorded level since records began due to the excessive emission of carbon dioxide from the burning fossil, resulting in the increasing of global temperatures and uncontrollable impacts on the world climate [1,2]. Therefore, development of efficient and economical technology for CO_2 capture and utilization from the burning fossil is highly desired. To address this issue, a growing number of researchers have devoted themselves to the field of CO_2 capture and utilization using different sorbent materials or technologies, such as amine-based solvent [3–6], superbase/protic polar solvent system [7], ionic liquids (ILs) [8–12], and so on. Among which protic ionic liquids (PILs) prepared through the stoichiometric neutralization reaction of certain Brønsted acids and Brønsted bases were widely employed as an absorbent and catalyst for CO_2 capture, activation, and transformation [13–17], due to their advantages such as easy preparation, tunable physicochemical characteristics, and good reactivity with CO_2. For example, 1,8-diazabicyclo[5.4.0]undec-7-enium 2-methylimidazolide ([DBUH][MIm]) PIL designed by Ma et al. has been recently used as both catalyst and solvent for the cyclization of CO_2 with propargylic amines to form the corresponding 2-oxazolidinones, and the further study on the mechanism of CO_2 transformation by employing the DFT method revealed that [DBUH][MIm] could capture CO_2 to form the ion pair [DBUH][MIm-CO_2], in which CO_2 was activated by having more negative charge on the O atom [15]. Actually, CO_2 could be activated through the formation of carbamate or alkyl carbonate with Lewis basic nitrogen species [7,15,17,18]. Consequently, the captured CO_2 by ILs also could be considered as the activated form of CO_2, which could render this system suitable for accomplishing chemical transformation of CO_2 under low pressure to avoid an additional desorption step [18]. For instance, 1,1,3,3-tetramethylguanidinium imidazolide ([TMGH][Im]) PIL has been served as an excellent absorbent for a highly efficient and reversible CO_2 capture through the reactivity between $[Im]^-$ anion and CO_2 in our recent work [19], which also has been successfully used as catalyst for the carboxylative cyclization of 2-aminobenzonitriles with CO_2 at atmospheric pressure and room temperature [17], and the reaction mechanism proved by *in situ* FT-IR and NMR spectroscopy indicated that t he interactions of

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[TMGH][Im] with CO_2 were of great help for CO_2 activation and the [TMGH][ImCOO] could be regarded as an activated state of CO_2 in the reaction. That is to say, the CO_2 absorption behavior of PILs, such as interactions between CO_2 with PILs, the rate of CO_2 absorption, and absorption capacity of CO_2, may have close relevance with the CO_2 activation and its subsequent transformation [15–19]. Therefore, the studies on the CO_2 absorption behavior of PILs are important because they not only relate to the CO_2 capture, but also to the CO_2 activation and its subsequent transformation.

As is well known, the alkalinity and physicochemical properties such as density and viscosity have a significant influence on the CO_2 absorption behavior of ILs. For example, Wang et al. [14,20] studied the effect of the alkalinity on the CO_2 absorption capacity of azole-based functionalized ILs by using the p K_a value of the anion to characterize their alkalinity, and found the absorption capacity of CO_2 was related to the p K_a value of the anion. However, due to the p K_a values of the anion from the literature measured in different solvent such as DMSO and water, it is difficult to evaluate the effect of the alkalinity on the absorption capacity accurately [14,20]. Moreover, physicochemical properties of functionalized ILs such as density and refractive index, reflecting the free space or free volume [21–23], also can affect the CO_2 absorption behavior. In addition, high viscosity of functionalized ILs will block the diffusion velocity of CO_2, which further influences the CO_2 capture and activation [24–26]. On the other hand, solubility parameter of ILs obtained from the activation energy for viscous flow is also related to CO_2 solubility [27–29]. Therefore, proper knowledge about the alkalinity and physicochemical properties of functionalized ILs may have a significant influence on CO_2 capture and its subsequent transformation, which also can provide guidance for CO_2 conversion using the captured CO_2 as a carbonyl source.

The aim of our present work is to select the suitable PILs for efficient CO_2 capture with high absorption capacity and great absorption rate. Herein, we select four azole-based PILs as the example, namely 1,5-diazabicyclo[4.3.0]non-5-enium pyrazolide ([DBNH][Pyr]), 1,5-diazabicyclo[4.3.0]non-5-enium imidazolide ([DBNH][Im]), 1,8-diazabicyclo[5,4,0]undec-7-enium pyrazolide ([DBUH][Pyr]), and 1,8-diazabicyclo[5,4,0]undec-7-enium imidazolide ([DBUH][Im]), which have potential application prospect in transformation of CO_2 and can be readily prepared by equimolar neutralization reaction of DBU or DBN with imidazole (Im) or pyrazole (Pyr). The alkalinity of the studied PILs was measured by potentiometric titration method [30–33]. The physicochemical properties associated with the behavior of CO_2 capture including density (ρ), viscosity (η), and refractive index (n_D) were determined at 298.15-328.15 K. It must be pointed out that ρ and η of [DBUH][Im] used in the present work come from our previous report [34]. Based on the experimental data and thermodynamic theory, thermal expansion coefficient (α_P), the activation energy for viscous flow (E_η), and solubility parameter of PILs (δ_{IL}) were calculated. Then, the influence of the type of anion and cation on the alkalinity and physicochemical properties were discussed. Furthermore, the CO_2 absorption behavior of the studied PILs was evaluated at 298.15 K, and the absorption mechanism was proved by FT-IR and ^{13}C NMR spectra. Accordingly, the effect of the alkalinity and physicochemical properties on CO_2 absorption behavior of above PILs was analyzed in detail aiming to give guidance for their further application of the captured CO_2. Finally, the enthalpy of CO_2 absorption for the azole-based PILs with higher CO_2 capture capacity and greater absorption rate was deduced according to the CO_2 absorption capacity at 298.15-323.15 K and van't Hoff's equation.

2. Experimental section and computational details

2.1. Preparation and characterization of azole-based PILs

1,8-Diazabicyclo[5.4.0]undec-7-ene (99%), 1,5-diazabicyclo [4.3.0]non-5-ene (99%), imidazole (99%), and pyrazole (99%) were all purchased from Aladdin Reagent Co., Ltd. Hydrochloric acid (36.5%) was purchased from Sinopharm Chemical Regent Co., Ltd. Carbon dioxide with a minimum purity of 99.99 mol% and high purity nitrogen with a minimum purity of 99.999 mol% were both supplied from Shanghai Pu Jiang Specialty Gases Co. Ltd.

[DBNH][Pyr], [DBNH][Im], [DBUH][Pyr], and [DBUH][Im] were synthesized by equimolar neutralization reaction of DBN or DBU with Pyr or Im, respectively [14,15,34,35]. In a typical synthesis of [DBNH][Pyr], 0.25 mol pyrazole was divided into several parts and added into 0.25 mol DBN in batches under vigorous stirring at room temperature for 24 h. Then the obtained PILs were dried under vacuum at 333.15 K for at least 24 h to remove possible trace of water. The water content of these azole-based PILs was determined with a Karl Fisher Coulometric Titration (Mettler Toledo C20S) and found to be less than 1000 ppm. The chemical structure of these azole-based PILs was characterized by using ^1H NMR and FT-IR spectra, which were listed in Supporting information, among which ^1H NMR spectra was measured on a Bruker AVANCE III spectrometer (400 MHz), using chloroform-*d* as a solvent, and FT-IR spectra was obtained by using a Nicolet 6700 Fourier transform infrared spectrometer equipped with ATR accessory.

2.2. Characterization of the alkalinity of azole-based PILs

According to literature, the basicity dissociation constant p K_b values could use to characterize the alkalinity, which was determined by potentiometric titration method [30–33]. Consequently, the alkalinity of the studied PILs was characterized by comparison of their p K_b values in this work. For p K_b determinations, a stock solution (0.100 mol L^{-1}) of PILs was prepared in high-purity water. The solution was then titrated with aqueous HCl solution (0.100 mol L^{-1}). The pH value of the solution was measured using a calibrated glass electrode on a pH meter (Model pHS-25, Shanghai Precision Scientific Instrument) at 298.15 (±0.10) K. The titration curve of pH value versus titration volume (V) of aqueous HCl solution was plotted. The p K_b for each PILs was calculated using pH value and concentration of base ($[A^-]$)

Table 1
Alkalinity, physicochemical properties, and CO_2 absorption capacity of four azole-based PILs.

PILs	V_e (mL)	p K_b	$10^4\alpha_p$	δ_{IL} $(J\,cm^{-3})^{1/2}$[a]	CO_2 absorption capacity[b]	Equilibrium time (min)
[DBNH][Im]	41.0	5.3	9.5941	26.5	0.80	~60
[DBNH][Pyr]	20.0	2.5	9.7448	24.1	0.87	~30
[DBUH][Im]	41.5	5.5	9.2494	28.6	0.78	~90
[DBUH][Pyr]	19.8	2.8	9.6535	26.1	0.82	> 120

[a] at 298.15 K.
[b] Absorption was carried out at 298.15 K, mole CO_2 per mole PIL.