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Reversible absorption of CO_2 by diethylenetriamine hydrochloride and ethylene glycol mixtures with high capacity and low viscosity

Shidong Tian[a], Yucui Hou[b], Weize Wu[a,*], Shuhang Ren[a], Jianguo Qian[a]

[a] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China*
[b] *Department of Chemistry, Taiyuan Normal University, Taiyuan 030031, China*

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ABSTRACT

In this work, three kinds of ammonium salts containing chloride ion [DETA]·*n*Cl (*n* = 1, 2, 3) were synthesized via the reactions between diethylenetriamine (DETA) and hydrochloric acid. And ethylene glycol (EG) was chosen as a solvent to dissolve [DETA]·*n*Cl to prepare liquid hybrid absorbents for the capture of CO_2. Effects of amount of chloride ion, absorption temperature, CO_2 partial pressure and [DETA]·Cl concentration on the absorption of CO_2 were systematically studied. It has been found that [DETA]·Cl (1) + EG (2) (mole ratio of EG to [DETA]·Cl $R = 4.0$) shows a high absorption capacity of CO_2. The mole ratio of CO_2 to [DETA]·Cl could reach 0.765 (0.0868 g CO_2/g absorbent) at 50 °C under atmospheric pressure. Importantly, the viscosity of [DETA]·Cl (1) + EG (2) ($R = 4.0$) is quite low (105.3 mPa s) even when it is saturated with CO_2 at 50 °C. Finally, [DETA]·Cl (1) + EG (2) ($R = 4.0$) could be reused to absorb CO_2 for five times without obvious loss of absorption capacity. The result indicates that [DETA]·Cl (1) + EG (2) is a promising reversible absorbent for the capture of CO_2.

1. Introduction

In recent years, the emission of carbon dioxide (CO_2) has caused serious greenhouse effect, which results in global warming and climate change. As a result, the capture and storage of CO_2 have drawn much attention all over the world. Currently, there are many absorbents developed for the capture of CO_2 [1–8]. For example, traditional liquid absorbents can be divided into physical absorbents, such as methanol and dimethylether of polyethylene glycol, and chemical absorbents, such as a variety of amines. Besides, solid absorbents, membranes and ionic liquids (ILs) are also applied for the capture of CO_2. Compared with physical absorbents, chemical absorbents show much higher absorption capacity of CO_2. However, the high volatility of amines may cause secondary environmental pollution and waste of resources. How to decrease the volatility of amines has drawn much concern.

It was reported that chloride ion could interact with amines via forming hydrogen bond, and the interactions could be strengthened when the amine was protonated [9–11]. Huang et al. dissolved monoethanolamine in hydroxyl imidazolium based IL containing chloride ion, and they found that the thermal stability of monoethanolamine during CO_2 capture could be enhanced. In addition, the loss of monoethanolamine decreased dramatically for the reason that there are strong interactions between amine and chloride ion [11]. Clyburne et al. found that tetradecyl(trihexyl)phosphonium chloride could lower the vapor pressure of diethylenetriamine significantly [12]. It was also reported that hydrogen bond could be formed between chloride ion and hydroxyl protons [13]. Rogers et al. studied the mechanism of cellulose dissolution in 1-n-butyl-3-methylimidazolium chloride ([Bmim]Cl), and they proposed that the solvation of cellulose by [Bmim]Cl was due to the formation of hydrogen bond between carbohydrate hydroxyl protons and chloride ion [13]. Li et al. found 1-methylimidazolium chloride ([Mim]Cl) could decrease the vapor pressures of water and alcohols due to the diluting effect of IL and the affinity of IL with solvent [14]. Therefore, the interactions between chloride ion and amino or hydroxyl group of molecules can reduce the volatility of molecule solvents.

Mixing amines in ILs containing chloride ion is much helpful to the capture of CO_2. However, the volatility of amines could not be ignored even when they are dissolved in ILs containing chloride ion. For example, monoethanolamine (MEA) – 1-(3-hydroxylpropyl)-3-methylimidazolium chloride ([C_3OHmim]Cl) lost more than 20 wt% of its weight under vacuum at 70 °C for 24 h [11]. In order to further reduce their volatility, amines could be protonated as mentioned earlier. As we know, the amines could be protonated via simple reactions between amines and hydrochloric acid. The products, which are ILs (with low melting point) or ammonium salts (with high melting point), reasonably show quite lower volatility than that of amines.

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[*] Corresponding author. Tel.: +86 10 64427603; fax: +86 10 64427603.
E-mail address: wzwu@mail.buct.edu.cn (W. Wu).

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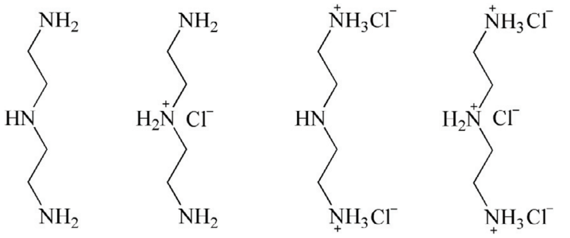
DETA [DETA]·Cl [DETA]·2Cl [DETA]·3Cl

Fig. 1. Chemical structures of [DETA]·*n*Cl ($n = 0, 1, 2, 3$).

Table 1
State of [DETA]·*n*Cl ($n = 1, 2, 3$) (1) + EG (2) hybrid absorbents at 50 °C.

[DETA]·*n*Cl	Mole ratio of EG to [DETA]·*n*Cl					
	$R^a = 1.0$	$R = 2.0$	$R = 3.0$	$R = 4.0$	$R = 5.0$	$R = 6.0$
[DETA]·Cl	s[b] + l[c]	s + l	l	l	l	l
[DETA]·2Cl	s + l	s + l	s + l	s + l	s + l	l
[DETA]·3Cl	s + l	s + l	s + l	s + l	s + l	s + l

[a] *R* stands for the mole ratio of EG to [DETA]·*n*Cl ($n = 1, 2, 3$).
[b] s: solid.
[c] l: liquid.

In this work, three kinds of ammonium salts containing chloride ion were synthesized, which are diethylenetriamine hydrochloride ([DETA]·Cl), diethylenetriamine bis(hydrochloride) ([DETA]·2Cl) and diethylenetriamine tri(hydrochloride) ([DETA]·3Cl). The chemical structures of [DETA]·*n*Cl ($n = 0, 1, 2, 3$) are shown in Fig. 1. Usually, the capture of acidic gas by liquid absorbents is more efficient than that by solid absorbents for the excellent mass transfer between liquid and gas phases. For solid state of the ammonium salts, choosing a proper solvent is necessary. Water is a common solvent, but the evaporation of water in the process of regeneration would cost much energy. As non-aqueous solvent, ethylene glycol (EG), which was reported as solvent of methyldiethanolamine [15], diethanolamine [16] and diisopropanolamine [17] for the capture of CO_2, has quite low vapor pressure. As a result, the energy cost would be decreased significantly when EG was used as the solvent. Hence, in this work, EG was also chosen as the solvent of [DETA]·*n*Cl. And then, CO_2 absorption behaviors in the hybrid absorbent and regeneration of the hybrid absorbent were systematically studied. Finally, viscosity of the hybrid absorbent during the absorption of CO_2 was also investigated.

2. Materials and method

2.1. Materials

CO_2 (99.995%) and N_2 (99.999%) were obtained from Beijing Haipu Gases Co., Ltd. (Beijing, China). Diethylenetriamine (DETA) was supplied by Aladdin Chemical Co., Ltd. (Shanghai, China). Analytical reagent hydrochloric acid and EG were obtained from Beijing Chemical Works (Beijing, China).

2.2. Synthesis of [DETA]·nCl (n = 1, 2, 3)

[DETA]·Cl used in this work was synthesized via the reaction between DETA and equimolar hydrochloric acid following the literatures [18,19]. After the reaction between DETA and hydrochloric acid finished, the solvent was removed by a rotary evaporator at 80 °C, and then the product was dried under vacuum at 80 °C for 48 h. [DETA]·2Cl and [DETA]·3Cl were synthesized in a similar way by changing the mole ratio of DETA to hydrochloric acid. The structures of [DETA]·*n*Cl ($n = 0, 1, 2, 3$) were confirmed by ^{13}C NMR spectra (Bruker AM 600 MHz, D_2O), and the result is shown in Fig. S1. The final products were stored in a desiccator avoiding the absorption of moisture from the atmosphere.

2.3. Volatility of [DETA]·nCl (n = 1, 2, 3)

The volatility of [DETA]·*n*Cl ($n = 1, 2, 3$) was studied by determining the weight loss of [DETA]·*n*Cl ($n = 1, 2, 3$) under vacuum at 80 °C. In order to investigate the effect of chloride ion on the volatility of amines, the weight loss of DETA was also studied. Taking [DETA]·Cl as an example, 5.0 g [DETA]·Cl was loaded in a 50 cm^3 conical flask, and then the conical flask was put in a vacuum drying oven at 80 °C. The weight of the conical flask and [DETA]·Cl was measured at regular intervals by an analytical balance (BS 224S, Sartorius) with a precision of 0.1 mg. [DETA]·Cl remained in the conical flask could be calculated by subtracting the weight of conical flask from the total weight of conical flask and [DETA]·Cl. The other experiments were carried out in a similar way as mentioned above.

2.4. Preparation of the hybrid absorbents

Eighteen samples of [DETA]·*n*Cl ($n = 1, 2, 3$) (1) + EG (2) with $R = 1.0$, 2.0, 3.0, 4.0, 5.0 and 6.0 (*R* stands for the mole ratio of EG to [DETA]·*n*Cl ($n = 1, 2, 3$)) were prepared in this work. The states of the mixtures are shown in Table 1, and the hybrid absorbents for the capture of CO_2 are shown in Table S1. All of the mixtures were prepared by an analytical balance (CPA 1003S, Sartorius) with a precision of 1 mg. After blending well, the samples were stored in a desiccator.

2.5. Absorption and desorption of CO₂

The absorption and desorption of CO_2 were carried out at ambient pressure following the literature [18]. The schematic diagram of the apparatus is shown in Fig. S2, which mainly consisted of a CO_2 gas cylinder, a rotameter, a test tube (15 mm × 150 mm), a constant temperature water (or oil) bath. The temperatures of the water (or oil) bath were maintained within ±0.5 °C.

In a typical absorption experiment, about 5.0 g hybrid absorbent was loaded in the test tube, and then a gas stream of 100 cm^3/min CO_2 was bubbled through the IL at desired temperatures. The flow rate of CO_2 was controlled by a rotameter, which was calibrated by a soap film fluid meter. Weight of the test tube was measured at regular intervals by an analytical balance (BS 224S, Sartorius) with a precision of 0.1 mg. And then the solubility of CO_2 in the absorbent could be calculated based on the weight increase. The desorption of CO_2 was carried out on the same device. In a typical desorption experiment, a gas stream of 100 cm^3/min N_2 was bubbled through the CO_2-saturated absorbent to accelerate the release of CO_2 at desired temperatures. The amount of CO_2 left in the absorbent could be calculated in a similar way as mentioned above. Measurements of the viscosity of the hybrid absorbent during the absorption of CO_2 were carried out following the literature [20].

3. Results and discussion

3.1. Volatility of [DETA]·nCl (n = 0, 1, 2, 3)

Fig. 2 shows the weight loss of [DETA]·*n*Cl ($n = 0, 1, 2, 3$) under vacuum at 80 °C. As can be seen from the figure, DETA becomes more stable when it changes into ammonium salt containing chloride ion. For example, the weight loss of DETA, [DETA]·Cl, [DETA]·2Cl and [DETA]·3Cl are 16.03 wt%, 1.01 wt%, 0.12 wt% and 0.09 wt% under vacuum at 80 °C for 30 h, respectively. Among these four compounds, [DETA]·*n*Cl ($n = 1, 2, 3$) are solid ammonium salts while DETA is liquid organic amine. The formation of ammonium salts containing chloride ion, where exists both hydrogen bond and

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