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Regeneration performance and absorption/desorption mechanism of tetramethylammonium glycinate aqueous solution for carbon dioxide capture

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ABSTRACT

Tetramethylammonium glycinate ($[N_{1111}][Gly]$) aqueous solution has a good absorption ability for CO_2 capture. In this paper, the desorption performance and mechanism were investigated. To explore the regeneration performance of the CO_2-saturated $[N_{1111}][Gly]$ aqueous solution, thermal regeneration under atmospheric pressure was used by varying the regeneration temperature from 373 to 403 K and the $[N_{1111}][Gly]$ concentration from 5% to 30%. The effect of regeneration cycles on regeneration efficiency was also determined. The interaction between CO_2 and $[N_{1111}][Gly]$ aqueous solution was explored by ^{13}C Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectrometry (IR). Results showed that 15% $[N_{1111}][Gly]$ aqueous solution had more preferable desorption performance than the other concentrations in the range of the investigation. The regeneration efficiency of the CO_2-saturated solution increased with increasing regeneration temperature from 373 to 383 K. When the temperature was above 383 K, it had little influence on the regeneration efficiency but still enhanced the desorption rate of CO_2. The regeneration efficiency and the desorption rate decreased slightly during four regeneration cycles. In CO_2 capture and release process, $[N_{1111}][Gly]$ only played a transitory role to stabilize the carbonate/bicarbonate by sequestering and providing protons. CO_2 desorption kinetics could be expressed by Weibull equation: $\eta_t/\eta_\infty = 1 - e^{-(t^m/\beta)}$.

1. Introduction

Carbon dioxide (CO_2) removal from post-combustion flue gas is of great importance for greenhouse gas (GHG) control, since it consists of 83% GHG emissions (Figueroa et al., 2008). The most used technologies for this purpose are based on absorption with aqueous amine solutions, due to their advantages of low cost, high efficiency, and good absorption capacity (Herzog, 1999). However, the degradation and volatilization of alkanolamine contribute to the solvent loss and equipment corrosion, which not only increase the cost of the process but also do harm to the environment (Lepaumier et al., 2009; Strazisar et al., 2003). Thus, scientists and engineers began to develop and design new kinds of solvents for CO_2 capture recycle and green processing (Anderson et al., 2007).

Ionic liquids (ILs) offer a new opportunity for addressing this challenge to develop novel CO_2 capture systems because of their unique properties (Hillesheim et al., 2012; Ren et al., 2012). However, conventional ILs are just limited to physical absorption, and their solubility of CO_2 is low (Huang and Rüther, 2009). In order to introduce chemical reaction, a variety of ILs were integrated with ions incorporating functional groups (Lu et al., 2012; Zhang et al., 2013c). Natural occurring amino acids (AA), which are easily obtained, bio-compatible and bio-degradable, are considered as an alternative for their amino moiety, thereby have drawn attention to new ILs design (Xue et al., 2011). A series of AA based ILs (AAILs) were prepared and tested for CO_2 capture (Fukumoto et al., 2005; Zhang et al., 2006). Since pure AAILs have high viscosity, the delivery of IL and the gas–liquid mass transfer in the absorption process are seriously affected.

Fortunately, these AAILs are highly soluble in water, and their aqueous solution owns low viscosity and high CO_2 capture capacity. According to the research of Zhang et al. (2010), $[N_{1111}][Gly]$ aqueous solution exhibited a good CO_2 absorption ability. The CO_2 loading of the saturated solution increased from 0.169 to 0.601 mol CO_2/mol IL as the mass fraction of $[N_{1111}][Gly]$ in the solution decreased from 100% to 30%. It had been revealed in our group that

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the absorption rate of CO_2 into 30% $[N_{1111}][Gly]$ solution was much higher than that of 30% TEA and 30% DEA, and only slightly lower than that of 30% MEA (Jing et al., 2012). Moreover, as the mass fraction of $[N_{1111}][Gly]$ in the solution decreased from 30% to 10%, CO_2 loading of the saturated solution increased from 0.601 to 0.721 mol CO_2/mol IL.

Besides absorption characteristics, regeneration performance is also a quite important criterion for CO_2 absorbent selection, especially in regards to the energy penalty in the regenerator. The regeneration performance of pure AAILs was reported in many literatures (Peng et al., 2013; Xue et al., 2011; Zhang et al., 2006). For example, Peng et al. (2013) reported that 90% of the total absorbed CO_2 was desorbed from [AEMP][Gly] solution, and the absorption rate and capacity did not significantly decline after five absorption/desorption cycles. To our knowledge, there were only a few literatures about regeneration performance of AAILs aqueous solution. Zhang et al. (2013a) reported the regeneration performance of AAILs activated with MDEA. The results revealed that most of the absorbed CO_2 in the liquid phase was released through thermal regeneration, and a higher regeneration temperature led to a larger release amount of CO_2. Our previous study (Guo et al., 2013) found that the regeneration efficiency of [Hmim][Gly] aqueous solution in turn was 96.7%, 95.0% and 88.8% for the first, the second, and the third cycle of regeneration, respectively, with a regeneration temperature of 338 K and a regeneration time of 90 min. The results were inconsistent with that of the other imidazolium-based ILs from literatures (Lu et al., 2011), which reported that the recovered ILs recycled for CO_2 uptake (four cycles) without observed loss of CO_2 absorption rate and absorption loading.

On the other hand, CO_2 absorption/desorption mechanisms in AAILs with and without water are different. The property of the products will directly affect the regeneration performance. For pure AAILs, some researchers reported that one CO_2 molecule combined with two IL molecules to form a neutral carbamate with an ammonium dication (Zhang et al., 2006). This mechanism was called 1:2 mechanism (Gurkan et al., 2010). Brennecke and Gurkan (2010) and Mindrup and Schneider (2010) suggested, based on both experimental observations and computational results that, in dry conditions, AAILs captured CO_2 as carbamic acid rather than as carbamate, and the resulting molar capture capacity would increase by 100% over a carbamate-type mode. Zhang et al. (2006) reported the CO_2 absorption capacity at equilibrium was half molar of the pure $[P(C_4)_4][AA]$. In the presence of water (1%, mass), this IL could absorb equimolar amounts of CO_2. In their work, the results of IR and ^{13}C NMR spectrum showed that, in CO_2-saturated $[P(C_4)_4][AA]$ aqueous solution, there did not contain a new peak or resonance that corresponding to the formation of a carbamate carbonyl (carbon), suggesting that the absorption/desorption mechanism was different to that of the pure AAILs.

Thus, in the present work, the regeneration performance of CO_2-saturated $[N_{1111}][Gly]$ aqueous solution, with mass fractions from 5% to 30%, was studied. The effects of regeneration temperature and regeneration cycles on CO_2 desorption rate and regeneration efficiency were also determined. The CO_2 absorption/desorption mechanism involving $[N_{1111}][Gly]$ aqueous solution was discussed through the spectra of ^{13}C NMR and IR. And the desorption kinetics of CO_2-saturated $[N_{1111}][Gly]$ aqueous solution was modeled using Weibull equation.

2. Experimental

2.1. Chemicals

$[N_{1111}][Gly]$ (purity >99.0%) was obtained from Lanzhou Greenchem ILS, LICP, CAS (China). The aqueous solution was prepared by using distilled water that had been further degassed by boiling before use. The pure CO_2 (purity >99.999%) was obtained from Fujian Nanan Chenggong Gas Co., Ltd (China).

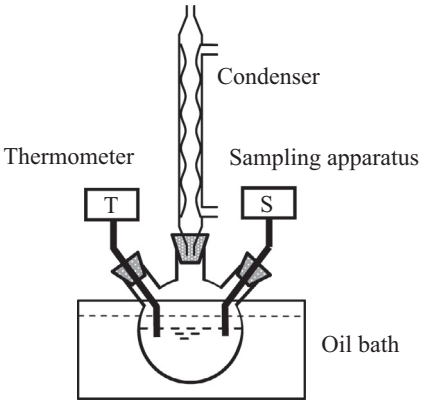

Fig. 1. Experimental apparatus for CO_2 regeneration.

2.2. CO_2 regeneration experiments

Before regeneration, the $[N_{1111}][Gly]$ aqueous solutions were saturated with CO_2 at 303 K and atmospheric pressure. The regeneration apparatus is depicted in Fig. 1. A three-necked bottle (500 mL) placed in oil bath was fed with 200 mL saturated absorbing solution. The temperature of the oil bath (the regeneration temperature, T_b) was maintained at a certain value. The whole regeneration was performed at atmospheric pressure.

After a certain period of thermal regeneration, 1 mL solution was sampled to measure the residual CO_2 concentration in $[N_{1111}][Gly]$ aqueous solution using the sulfuric acid hydrolysis method (McClatchie et al., 1977). The essence of this method was similar to the principal of the improved Austrian Gas Analyzer. As shown in Fig. 2, 5 mL sulfuric acid solution (3 mol L^{-1}) was injected into the reaction bottle, and then 1 mL sample solution was added into the inner bottle. The sealed liquid tube was filled with a certain amount of CO_2-saturated solution (saturated sodium bicarbonate). Adjust the liquid level in the sealed liquid tube to keep level with the eudiometer, and note the eudiometer reading as V_1. Oscillate the reaction bottle to release the CO_2 in the solution. Re-adjust the liquid level in the sealed liquid tube to keep level with the eudiometer, and note the eudiometer reading as V_2. CO_2 concentration and CO_2 desorption rate can be calculated as follows:

$$n_{CO_2} = \frac{P(V_2 - V_1)}{RT_r V_0} \quad (1)$$

$$N = \frac{\Delta n_{CO_2}}{\Delta t} \quad (2)$$

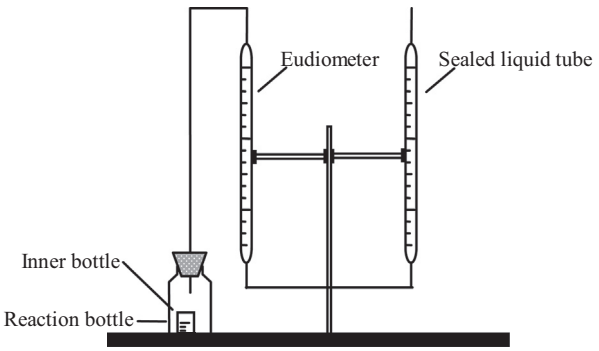

Fig. 2. Experimental apparatus for CO_2 concentration measurement using acid hydrolysis method.