Absorption performance of (CO$_2$ + N$_2$) gas mixtures in amino acid ionic liquids promoted *N*-methyldiethanolamine aqueous solutions

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A B S T R A C T

Amino acid ionic liquids (AAILs) including 1-butyl-3-methylimidazolium glycinate ([Bmim][Gly]), 1-butyl-3-methylimidazolium L-lysinate ([Bmim][Lys]) and tetramethylammonium glycinate ([N$_{1111}$][Gly]) were used to enhance the absorption of CO$_2$ in *N*-methyldiethanolamine (MDEA) aqueous solutions. The mole fractions of CO$_2$ in N$_2$ + CO$_2$ gas mixtures ranged from 0.2 to 1.0. The mass fractions of MDEA and AAILs respectively ranged from 0.300 to 0.400 and 0.050 to 0.100. The absorption capacity and absorption rate under series of conditions were presented and the influences of CO$_2$ partial pressure and the types of AAILs on the absorption performance were demonstrated.

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1. Introduction

In recent decades, atmospheric levels of CO$_2$ have increased rapidly due to the utilization of great amount of fossil fuel. The reduction of CO$_2$ emission became a global issue [1–3]. There are several technologies available for removing CO$_2$ from gas streams [4,5], such as chemical absorption, physical absorption, cryogenic separation, membrane separation and biological fixation. Among these technologies, chemical absorption using alkanolamine aqueous solutions as absorbents was widely used for capturing CO$_2$ from power plant flue gas, natural gas, synthetic gas and hydrogen gas streams [6–9]. However, traditional alkanolamine aqueous solutions have some disadvantages like high corrosivity and high energy cost of regeneration [10–12]. Therefore, development of new absorbents with high absorption capacity, high reaction rate, low corrosivity and low energy cost in regeneration has become the focus of world attention. For example, the mixed aqueous solutions of *N*-methyldiethanolamine (MDEA) and a primary or a secondary alkanolamine were considered as effective absorbent applicable for industrial applications. As a tertiary alkanolamine, MDEA takes the advantages of high absorption capacity for CO$_2$, low corrosivity, low solution vapour pressure, low enthalpy of absorption and high resistance to thermal and chemical degradation. However, compared with primary and secondary amines, MDEA has slower reaction rate with CO$_2$ because it appears to

act only as a weak base to produce free OH$^-$ [13]. It's well documented that adding small amount of primary amine like monoethanolamine (MEA) into MDEA aqueous solution can overcome the aforementioned disadvantage of MDEA [14,15]. The blends of MEA and MDEA preserve the high rate of the reaction of MEA with CO$_2$ and the low enthalpy of the reaction of MDEA with CO$_2$, hence lead to higher absorption rates in the absorber column, yet lower heat of regeneration in the stripper section. Besides MEA, piperazine (PZ) is also able to enhance the absorption rate of CO$_2$ in MDEA aqueous solution. Kadiwala et al. [16] compared the absorption performance of CO$_2$ in MEA and PZ aqueous solutions, and found that PZ has greater capacity and much higher reaction rates than MEA. Ali et al. [17] investigated the solubility of CO$_2$ in PZ promoted MDEA aqueous solutions under series of temperatures and CO$_2$ partial pressures. Their results showed that the addition of PZ increased the solubility of CO$_2$, especially in the case of low CO$_2$ partial pressure. Xu et al. [18] also found that the addition of small amount of PZ is beneficial to CO$_2$ loading in MDEA aqueous solutions.

Another approach to enhance the absorption of CO$_2$ in MDEA aqueous solutions is to use the functionalized ionic liquids (FILs) as activators. The FILs have unique characteristics including wide liquid range, thermal stability, negligible vapour pressure, tunable physicochemical character and high CO$_2$ solubility [19–22]. The blends of FILs and MDEA preserve the desired property of FILs for CO$_2$ capture, but without many of their inherent drawbacks such as high viscosity [23–27]. Among FILs, the amino acid ionic liquids (AAILs) are considered to be the most promising activators to

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enhance the absorption rate of CO_2 in MDEA aqueous solution. In recent years, many studies have been focused on the absorption capacity and absorption rate of pure CO_2 in AAILs promoted MDEA aqueous solutions. For example, Zhang et al. [28] investigated the absorption performance of CO_2 in the tetramethylammonium glycinate ([N_{1111}][Gly]) promoted MDEA aqueous solutions at 298 K. They found that the increase in [N_{1111}][Gly] concentration has conflicting influence on the CO_2 absorption rate and determined the minimum and maximum apparent absorption rates at given MDEA concentration. Zhang et al. [29] investigated the absorption of CO_2 in [N_{1111}][Gly], tetraethylammonium glycinate ([N_{2222}][Gly]), tetramethylammonium L-lysinate ([N_{1111}][Lys]) and tetraethylammonium L-lysinate ([N_{2222}][Lys]) promoted MDEA aqueous solutions over a wide range of FILs concentrations and temperatures, and showed the influences of temperature and concentration on the absorption of CO_2. Gao et al. [30] investigated the influences of temperature, solution composition and pressure on CO_2 absorption in [N_{1111}][Gly]-MDEA aqueous solutions. They found that the absorption capacity increases greatly as the pressure grows when pressure is less than 60 kPa, however, it increases gradually with increasing pressure when the pressure is over 100 kPa. Very recently, Fu et al. [31–33] studied the absorption capacity and absorption rate of pure CO_2 in MDEA aqueous solutions respectively promoted by 1-butyl-3-methylimidazolium glycinate ([Bmim][Gly]), 1-butyl-3-methylimidazolium L-lysinate ([Bmim][Lys]) and [N_{1111}][Gly]. They determined the effects of temperature and solution concentration on absorption capacity and absorption rate. Moreover, they modelled the viscosities of carbonated MDEA-AAILs aqueous solutions and demonstrated both solution concentration and solution viscosity can significantly affect the absorption process and there exists competition between concentration and viscosity. Besides the absorption performance of pure CO_2, there are some studies concerning the absorption performance of $N_2 + CO_2$ mixtures in solutions containing ionic liquids. In particular, Kanakubo et al. [34] investigated the solubilities of $N_2 + CO_2$ in 1-butyl-3-methylimidazolium acetate ([BMIM][AcO]) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide ([BMIM][Tf_2N]) at atmospheric pressure. Lu et al. [35] studied the absorption of $CO_2 + N_2 + O_2$ gas mixtures (concentration of CO_2 is 15%) in 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4])-MEA aqueous solutions at atmospheric pressure. Zhang et al. [29] investigated the absorption of $N_2 + CO_2$ in [N_{1111}][Gly], [N_{2222}][Gly], [N_{1111}][Lys] and [N_{2222}][Lys] promoted MDEA aqueous solutions. Their results showed that the CO_2 partial pressure plays an important role in the absorption process, and negligible amount of N_2 can be simultaneously absorbed. The CO_2 loading increases with the increase of CO_2 partial pressure and the higher is the CO_2 partial pressure, the less time is needed to reach equilibrium absorption. However, the absorption performance of $N_2 + CO_2$ in [Bmim][Gly]-MEDA, [Bmim][Lys]-MDEA and [N_{1111}][Gly]-MDEA aqueous solutions have been rarely reported. The enhancement efficiencies of [Bmim][Lys], [N_{1111}][Gly] and [Bmim][Gly] are not yet clear, and the competition effects of solution concentration, solution viscosity and CO_2 partial pressure on absorption performance have not been well documented so far.

The main purpose of this work is to determine the effects of partial pressure, solution viscosity and solution concentration on the absorption performance of $N_2 + CO_2$ in [Bmim][Gly], [Bmim][Lys] and [N_{1111}][Gly] promoted MDEA aqueous solution, and demonstrate the promotion efficiencies of different AAILs. To this end, the time dependent absorption capacities of ($N_2 + CO_2$) in MDEA-[Bmim][Gly], MDEA-[Bmim][Lys], MDEA-[N_{1111}][Gly] aqueous solutions were measured under different CO_2 partial pressures and different solution compositions. The absorption rates under different operations were determined from the experiments. The competition among concentration, viscosity and partial pressure was determined.

2. Experimental

2.1. Materials

Chemicals used in this work are detailed in Table 1. They were used without further purification. An analytical balance (Jingtian FA1604A) with an accuracy of 0.1 mg was used to weigh all the required chemicals. CO_2 (purity by mole >0.999) and N_2 (purity by mole ≥0.99999) were purchased from the Jinglian Gas Supply Inc. The water contents (in mass fraction) of MDAE, MEA, [Bmim][Gly], [N_{1111}][Gly] and [Bmim][Lys] are respectively 0.06%, 0.15%, 0.26%, 0.18% and 0.28% (determined by using the Karl Fischer method, as stated by the supplier). It's worth noting the water contents may slightly differ from those reported by the supplier because the samples may be exposed to the air when they are in use. Aqueous solutions of MEDA-AAILs were prepared by adding doubly distilled water (Electrical resistivity >15 MΩ cm at 298 K) obtained from the Heal Force ROE (Reverse Osmosis Electro deionization)-100 apparatus and the water content in the studied compounds was accounted for upon solution preparation. Taking the purities and water contents into account, the uncertainties of the mass fraction of amines and AAILs are estimated as $u(w)$ = ±0.005.

2.2. Apparatus and procedure

The absorption performance was measured by the equipment composed of one high-pressure CO_2 tank, one high-pressure N_2 tank, two mass flow controllers (MFCs, manufactured by Beijing Seven-Star electronics Co., the accuracy is ±1%), one mass flow meter (MFM, manufactured by Beijing Seven-Star electronics Co., the accuracy is ±1%), one absorption bottle, one constant temperature water bath, one desiccator and one CO_2 analyser (manufactured by Germany Sensors Europe GmbH, the accuracy is ±2%). The CO_2 analyser measures the CO_2 concentration based on the Non-Dispersive Infrared (NDIR) technology. An IR detector in the analyzer can detect the intensity of IR light, and then convert it into CO_2 concentration by using the quantitative relationship between the amount of CO_2 in the gas sample and the detected intensity. The schematic diagram of the experiment is shown in Fig. 1. The absorption bottle (250 ml) was immersed into the thermostatic bath and the temperature of the solution can be regulated within 0.1 K. The rotational speed of the magnetic stirrer was fixed at 750 rpm. The equipment was designed to operate at atmospheric pressure (±2 kPa), and the total pressure of the ($CO_2 + N_2$) mixture is 100 kPa.

During the experiment, CO_2 and N_2 from high-pressure tanks were respectively inlet into the mass flow controllers to maintain constant flow rates v_{CO2} and v_{N2}, and then into the gas mixer.

Table 1
Sample description.[a]

Substance	Source	Purity	CAS No.
MDEA	Macklin Reagent	$w \geq 0.98$	105-59-9
MEA	Aladdin reagent	$w \geq 0.995$	141-43-5
[Bmim][Gly]	Shanghai Cheng Jie Chemical Co., Ltd	$w \geq 0.99$	1028361-04-7
[Bmim][Lys]	Shanghai Cheng Jie Chemical Co., Ltd	$w \geq 0.99$	1084610-48-9
[N_{1111}][Gly]	Shanghai Cheng Jie Chemical Co., Ltd	$w \geq 0.99$	55378-67-1

[a] Stated by the supplier; w denotes mass fraction.