

Evaluation of CO₂ absorption efficiency using amine/ionic liquid mixed absorbents for flue gas

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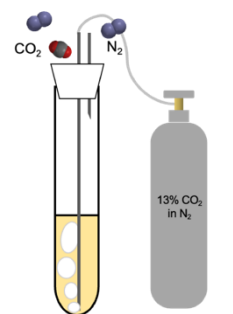
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Abstract

Carbon dioxide capture and storage (CCS) technology is a crucial strategy for mitigating global warming by reducing CO₂ emissions from stationary industrial sources. We have designed a diethylenetriamine (DET)-based absorbent molecule in which both terminal amine moieties are tertiary and the central amine is secondary. This configuration provides two proton-accepting tertiary sites, theoretically enabling the absorption of one mole of CO₂ per mole of amine through chemical interaction. However, experimental results showed that the amine efficiency—defined as the maximum CO₂ absorbed per mole of amine—did not exceed 0.5 mol-CO₂/mol-amine, which is significantly lower than expected. ¹H NMR and FTIR analyses suggested that some of the amines form the corresponding carbamic acids, which subsequently associate with unreacted amines through intermolecular hydrogen bonding. Recently, amine solutions utilizing ionic liquids as catalysts have been developed for CO₂ absorption, taking advantage of the high thermal stability, low vapor pressure, and easy recyclability of ionic liquids¹⁾. To dissociate such aggregation, we focused on using highly polar ionic liquids as solvents, thereby increasing the equilibrium CO₂ loading of DET. To further advance CCS technology, we have designed an efficient CO₂ capture system using DET ^{1,2)} mixed with hydroxyl-functionalized ionic liquids, HEMIMBF₄ or HEMIMTFSI.

Fig. 1 shows a schematic diagram of the apparatus used in all experiments. The CO₂ loading was determined by measuring the net weight increase of the absorbent during and after aeration of a simulated exhaust gas (13% CO₂ in N₂) into the solution. The amount of absorbed CO₂ was subsequently quantified.

First, the CO₂ absorption performance of **1** and ionic liquids was evaluated by adjusting the molar ratio to 1/1. As shown in Fig. 2, the absorbent solution of **1** and HEMIMBF₄ (1/1) remained heterogeneous before and after CO₂ absorption, with a CO₂ absorption capacity of 0.452 mol-CO₂/mol-amine, showing almost no improvement compared to neat amine (0.449 mol-CO₂/mol-amine). In contrast, the absorbent solutions of **1** mixed with HEMIMTFSI, BMIMTFSI, or OMIMTFSI (1/1), which became homogeneous upon CO₂ aeration, exhibited enhanced absorption performance compared to neat amine. Notably, the absorbent solution of



Gas type: 13% CO₂ in N₂
Flow rate: 100 mL/min

Fig. 1. Simple test tube setup for measuring CO₂ absorption

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1 and HEMIMTFSI demonstrated a CO₂ absorption capacity of 0.633 mol-CO₂/mol-amine, surpassing that of neat amine.

Furthermore, we compared the CO₂ absorption characteristics when increasing the molar ratio of OMIMTFSI and HEMIMTFSI to **1**. As shown in Fig. 2, no significant change in absorption capacity was observed with increasing molar ratio with OMIMTFSI. However, for HEMIMTFSI, the absorption capacity reached 1.10 mol-CO₂/mol-amine at a 1/5 ratio (**1**/HEMIMTFSI), which is nearly twice that of absorbent consisting of a 1/1 mixture of **1** and HEMIMTFSI. This enhancement is attributed to (1) a moderate increase in solution viscosity during CO₂ absorption in the ionic liquid, which facilitates gas–liquid mass transfer, (2) the formation of a carbonate species through the reaction of CO₂ with the hydroxyl group in the ionic liquid, and (3) the effective solvation of the CO₂ adducts, thereby suppressing the aggregation between the carbamate generated and unreacted amine **1**. These factors contribute to the enhanced CO₂ absorption efficiency of amine **1**.

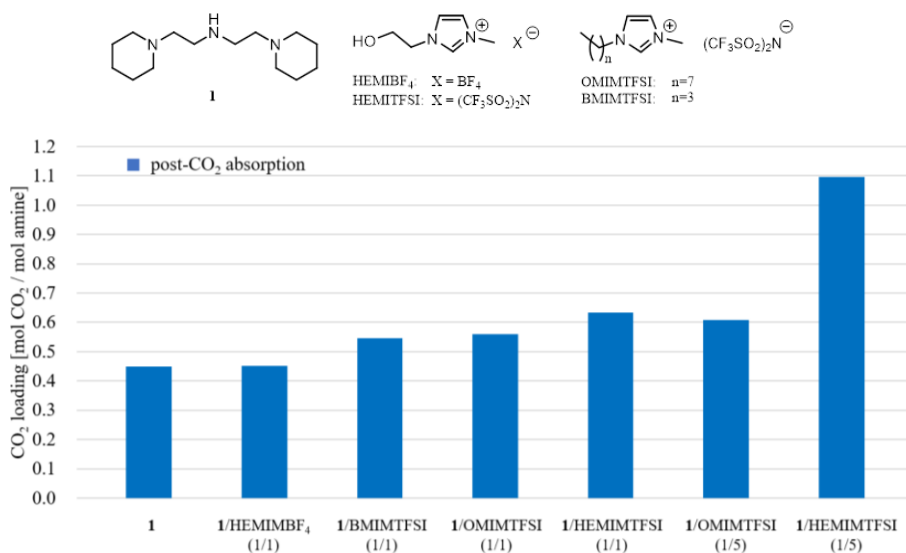


Fig. 2. Post-absorption CO₂ loading for neat liquid **1** and **1**/ionic liquid mixtures

References:

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Keywords: CO₂ absorption and desorption; amine-based absorbent; diethylenetriamines; ionic liquid; phase separation behavior