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Utilization of tertiary amine solutions and ultrasound irradiation for CO_2 desorption at low temperature in a process of CCS

CCSにおける二酸化炭素の低温脱離を目的とした第三級アミン溶液と超音波照射の利用

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1. Introduction

CCS(carbon dioxide capture and storage) is a technology of recovering carbon dioxide (CO_2) from exhaust gas of fired power plant and storing it in underground. Monoethanolamine (MEA) is mainly used as a chemical absorbent in CCS technology. MEA has several advantages compared to other alkanolamines such as high CO_2 absorption amount per unit weight and high CO_2 absorption rate [1]. MEA reacts with CO_2 and carbamate ion ($RNHCOO^-$) is generated according to Eq. (1). And HCO_3^- is also generated according to Eq. (2).

$$2RNH_2 + CO_2 \rightarrow RNH_3^+ + RNHCOO^- \quad (1)$$

$$RNH_2 + CO_2 + H_2O \rightarrow RNH_3^+ + HCO_3^- \quad (2)$$

(R: C_2H_5O, RNH_2: MEA)

After the CO_2 absorption from exhaust gas using MEA, CO_2 is recoverd from the MEA solution as pure CO_2 gas which is stored in undergraoud.

However, the drawback of MEA utilization is high cost because desorption of CO_2 from MEA solution (4.9M) requires high temperature of >110°C [2]. Therefore, it is necessary to find out new method to desorb CO_2 from amine solution at low temperature.

We have been focussed on ultrasound to desorb CO_2 from CO_2 adsorbed MEA solution at low temperatue. We clalified that deaerating action of ultrasound is available for desorption of CO_2(g) from CO_2(aq) in low concentration, 0.2M, of MEA solution at 25°C [3]. We also clalified that CO_2 desorption by ultrasound works at pH <8.2 because only CO_2(aq), the main species of CO_2 at these pH vaues, can be desorbed by ultrasound (**Fig. 1**).

In this study, we tried to use tertiary amine solution instead of primary amine, MEA, in the pesence of ultrasound. Normally, tertiary amine solution is lower CO_2 absorption rate than MEA solution. However, CO_2 absorption capacity, CO_2 mole per one mole of amine, of tertiary amine is higher than that of primary amine.

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CO_2 absorption reaction using tertiary amine solution is shown as Eq. (3).

$$R^1R^2R^3N + CO_2 + H_2O \rightarrow R^1R^2R^3NH^+ + HCO_3^- \quad (3)$$

Ultrasound can desorb CO_2(aq) as CO_2(g) from amine solution. However, directry desorption of CO_2 from CO_3^{2-}, HCO_3^-, and $RNHCOO^-$ is difficult for ultrasound. We consider that CO_2(g) can be desorbed continuously by the shift in the equilibrium of CO_2 toward the CO_2(aq) ($HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2(aq) + H_2O$). Therefore, we consider that dissociation constant (pKa) of tertiary amine solution regulates CO_2(g) desorption amount by ultrasound irradiation. Thus, we investigated the influence of pKa of tertiary amine on CO_2 desorption using ultrasound irradiation at low temperature. In this study, we used two tertiary amine solutions, triethanolamine (TEA) and N-Methyldiethanolamine (MDEA), which are different value of pKa, 7.85 (TEA) and 8.65 (MDEA) [4].

2. Experiment

CO_2-absorbed TEA solution (TEA-CO_2) and CO_2-absorbed MDEA solution (MDEA-CO_2) were prepared in a pressure vessel with 5.0 M tertiary amine solution (TEA or MDEA) under the condition of 0.5 MPa CO_2 gas for 12 h with stirring at 750 rpm. The absorption amount of CO_2 in the amine solution was determined from the change in the weight of the amine solution before and after CO_2 absorption. The desorption of CO_2 from the CO_2 absorbed amine solution was performed by ultrasound irradiation using an ultrasound generator (Kaijo, TA-4021) and a submersible transducer (28 kHz). A submersible transducer was placed at the bottom of a water-filled tank, and the flat-bottom flask containing TEA-CO_2 solution or MDEA-CO_2 solution (100 mL) was placed directly above the transducer. These solutions were irradiated by ultrasound for 15min at 20-25˚C. The reached power from transducer to te solution in the flask was 12W by calorimetrically method. The desorption ratio (%) of CO_2 gas was determined from the weight loss of the solution after the desorption experiment.

3. Results and discussion

Fig.2 shows CO_2 absorption amount of TEA and MDEA solution and the value was 154 g/L and 207 g/L, respectively. MDEA, which is heigher pKa value, showed higher CO_2 absorption amount than TEA. Fig.3 shows changes of CO_2 desorption amount by irradiation time of ultrasound. CO_2 desorption amount from TEA and MDEA solution was 71g/L and 36g/L, respectively. TEA, which is lower pKa value, shows lower CO_2 absorption amount but shows higher CO_2 desorption amount. CO_2 desorption ratio was caluculated by following formula.

CO_2 desorption ratio (%) = (CO_2 desorption amount / CO_2 absorption amount) $\times 100$.

CO_2 desorption ratio of TEA and MDEA is 46% and 17%, respectively. TEA can desorb almost half amount of CO_2 absorbed. From this result, the ultrasound can desorb CO_2 gas from TEA solution more efficiently than from MDEA solution. The difference of CO_2 desorption amount of TEA and MDEA solution may come from the difference of pH value of each solution. Fig.4 shows changes of pH value of each solution at CO_2 desorption process using ultrasound irradiation for 15 min. Before the ultrasound irradiation (0 min), TEA, which is lower pKa value, shows lower pH value than MDEA. The lower pH increases molar ratio of CO_2(aq) (Fig.1). Ultrasound can desorb CO_2(aq) as CO_2(g) from amine solution. Therefore, CO_2 desorption amount increased even at loe temperature using lower pKa tertiary amine solution and ultrasound irradiation.

Conclusion

The tertiary amine solution, which has lower pKa value, is more effective on CO_2 desorption combined with ultrasound irradiation. TEA shows high CO_2 desorption ratio of 46% for 15 min irradiation even at low temperature.

References

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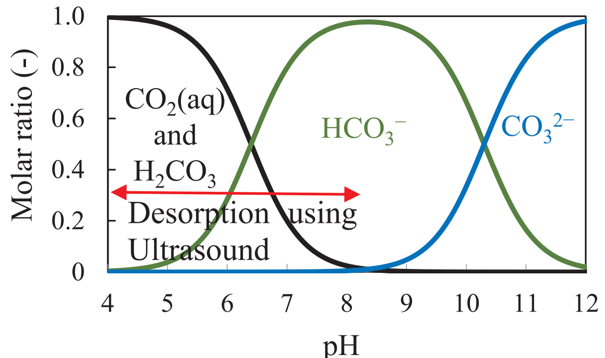

Fig.1 Relationship between chemical speciation of CO_2 and pH in solution at 25°C.

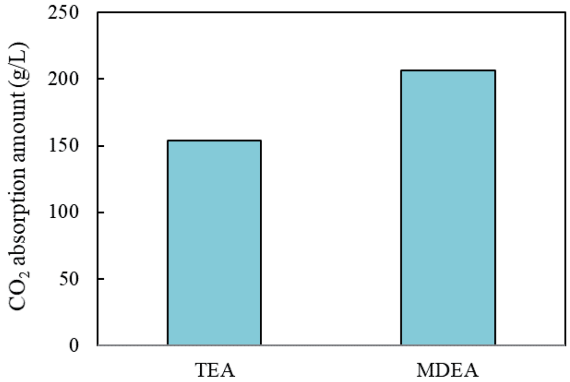

Fig.2 CO_2 absorption amounts of tertiary amine solutions (5.0 M, 200 ml, 20~25°C).

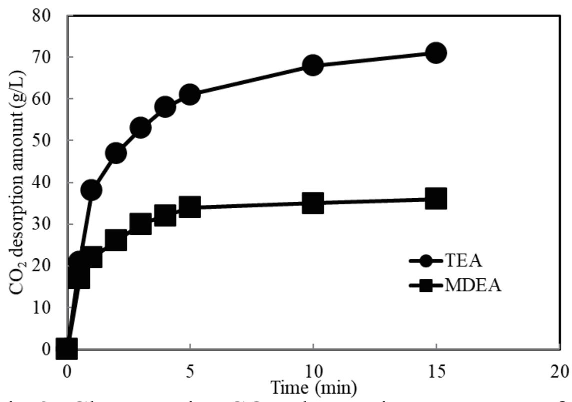

Fig.3 Changes in CO_2 desorption amount of each tertiary amine (5.0 M, 100 ml, 20-25°C).

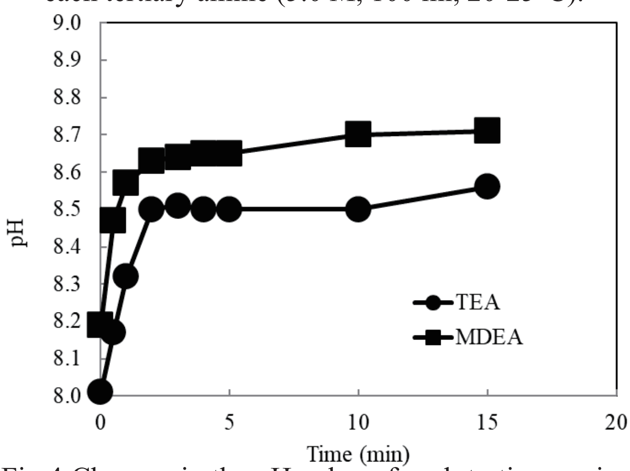

Fig.4 Changes in the pH value of each tertiary amine at CO_2 desorption process (5.0 M, 100 ml, 20-25°C).