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CO_2 desorption from tertiary amine solutions using ultrasound irradiation at low temperature

超音波を用いた第三級アミン溶液からの二酸化炭素の低温脱離

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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 pure CO_2 gas in underground. Therefore, solvents which have good ability for CO_2 capture and CO_2 release are required. Monoethanolamine (MEA) is mainly used as a chemical absorbent in CCS technology. The reason is that MEA can absorbe high CO_2 amount per unit weight and its CO_2 absorption rate is high[1]. Reaction formulae of MEA solution and CO_2 are shown below. CO_2 is absorbed as carbamate ion ($RNHCOO^-$) and carbonate ion.

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

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

(R: C_2H_5O, RNH_2: MEA)

CO_2 absorption by MEA is exothermic reaction. Therefore, recovering CO_2 from MEA solution throgh the inverse reactions of Eqs. (1) and (2) require heating. Desorption of CO_2 from MEA solution (4.9M) requires >110°C[2], which is related to high cost. Therefore, a new method for desorbing CO_2 from an amine solution at a low temperature must be developed.

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

We forcused on tertiary amine solution instead of primary amine solution because mechanics of reaction with CO_2 is different from that of primary amine. 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, directly desorption of $RNHCOO^-$ is difficult. Thus, we think that tertiary amine solutions, which does not generate carbamate ion, $RNHCOO^-$, were suitable for CO_2 desorption using ultrasound.

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Ultrasound can desorb CO_2(aq) as CO_2(g) from amine solution. We approched 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 investigated the influence of dissociation constant (pKa) of tertiary amine on CO_2 desorption using ultrasound irradiation. Normally, tertiary amine solution is lower CO_2 absorption rate than MEA solution. However, CO_2 absorption capacity, which is CO_2 mole per one mole of amine, of tertiary amine is higher than that of primary amine. In this study, we used triethanolamine (TEA) which has lower value of pK, 7.85 [4].CO_2 absrobed TEA was prepared under the different presure of 0.1MPa and 0.5MPa CO_2 gas to confirm the effect of pressure of CO_2 gas in absorption process for desorption ratio using ultrasound.

2. Experiment

5.0M TEA solution was adjusted using ion-ecchanged water. CO_2-absorbed TEA solution (TEA-CO_2) was prepared following two conditions. (1) CO_2 was absorbed to TEA solution under the condition of 0.1MPa. CO_2 was injected into 5.0M TEA solution at 100 ml/min for 6h. (2) CO_2 was absorbed to 5.0M TEA solution under the condition of 0.5MPa for 12 h with stirring at 750 rpm in a pressure vessel. 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 CO_2 desorption from the TEA-CO_2 solution was performed using 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 (50mL for 0.1MPa TEA-CO_2, 100 mL for 0.5MPa TEA-CO_2) 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.1 shows CO_2 absorption amount of TEA. When pressure is 0.1MPa, CO_2 absorption amount was 40 g/L. And high pressure of 0.5 MPa showed the amount of 154 g/L. CO_2 absorption amount by 0.5MPa showed aproxymatery 3.9 times higher than that by 0.1MPa. Next step, we dosorbed CO_2 from 0.1 MPa TEA-CO_2 solution and 0.5 MPa TEA-CO_2 solution using 28 kHz ultrasound for 15min. Fig.2 shows CO_2 desorption ratio of each TEA-CO_2 solution. CO_2 desorption ratio was caluculated by following formula.

CO_2 desorption ratio (%) = (CO_2 desorption amount / CO_2 absorption amount) ×100.

CO_2 desorption ratio of 0.1 MPa and 0.5 MPa TEA-CO_2 solution is 18% and 46%, respectively. This result comes from pH value of TEA after CO_2 absorption. 0.1 MPa TEA-CO_2 solution showed pH8.5 and 0.5 MPa TEA-CO_2 solution showed pH8.0. Ultrasound can desorb CO_2(aq) as CO_2(g) from TEA solution. CO_2(aq) can be the main species of CO_2 in the solution at pH <8.2. Therefore, 0.5 MPa TEA-CO_2 solution, which includs CO_2(aq), showed high CO_2 desorption ratio. Finally, we compared the CO_2 desorption amount and CO_2 desorption ratio of 0.1 MPa TEA-CO_2 solution (50 mL) using ultrasound (28 kHz) and stirring (1000 rpm) for 20 min (Fig.3). Ultrasound could desorb CO_2 farster than stirring. As these results, ultrasound has advantage even at low CO_2 absorption amount of TEA, 0.1 MPa TEA-CO_2 solution. In a presentation, we will show the results of the other tertiary amine solutions.

Conclusion

CO_2 desorption ratio of TEA solution under the condition of 0.1 MPa and 0.5 MPa was investigated. CO_2 desorption ratio was related to pH value of TEA solution after CO_2 absorption. We also evaluated the CO_2 desorption ratio of TEA solution using stirring and ultrasound. Utilization of ultrasound is more effective on CO_2 desorption.

References

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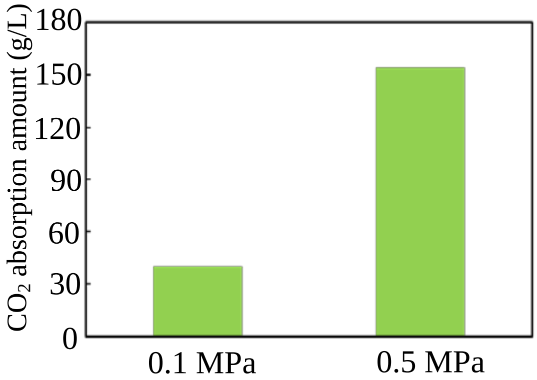

Fig.1 CO_2 absorption amount of TEA solution under the condition of 0.1 MPa and 0.5 MPa (5.0 M TEA, 20-25°C).

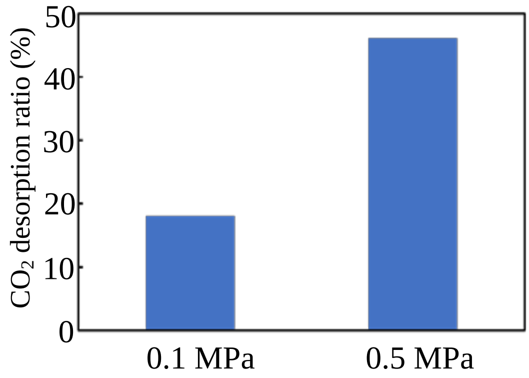

Fig.2 CO_2 desorption ratios of 0.1 MPa TEA-CO_2 solution and 0.5 MPa TEA-CO_2 solution using 28 kHz ultrasound for 15 min.

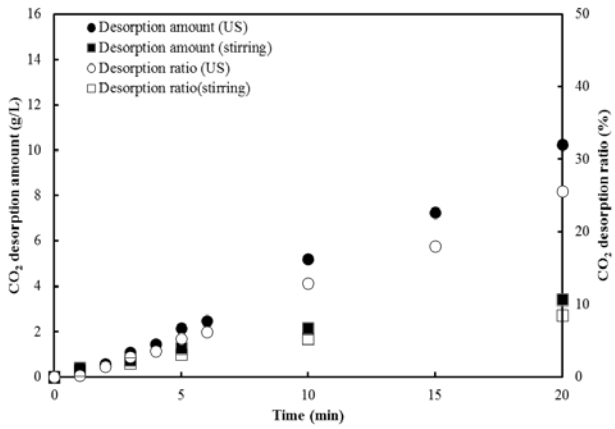

Fig.3 Changes in CO_2 desorption amount and CO_2 desorption ratio of 0.5MPa TEA-CO_2 using ultrasound and stirring (5.0 M, 50 ml, 20°C).