2P4-3

Enhancement of desorption amount of carbon dioxide gas from monoethanolamine solution using ultrasound and calcium chloride

超音波と塩化カルシウムを用いたモノエタノールアミン溶液からの CO_2 ガス脱離量の増進

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1. Introduction

Large amount exthoust of CO_2 gas is concern about global warming. Therefore, we have to abate emission of CO_2 gas from some places. Currently, carbon dioxide capture and storage (CCS) technologies are expected as a global warming measure. Monoethanolamine (MEA) has been used as an absorbent for capturing CO_2 from exhaust gas. Because MEA has several advantages over other alkanolamines: high CO_2 absorption amount per unit weight, high CO_2 absorption rate, and the low solvent cost.[1] However, high temperature of 120 °C is necessary to desorb CO_2 gas from MEA solution. When CO_2 is absorbed into MEA solution, carbamate ion ($RNHCOO^-$) is generated as a following reaction,

$$2RNH_2 + CO_2 \rightarrow RNH_3^+ + RNHCOO^-. \quad (1)$$
(R: C_2H_5O, RNH_2: MEA)

Also, chemical species of CO_2 in an aqueous solution are changed by pH of the solution. The species are mainly three: dissolved CO_2 gas (CO_2(aq)), HCO_3^-, and CO_3^{2-} (Fig. 1 and Eq. (2)–(4)).

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+ \quad (pKa_1 = 10.3) \quad (2)$$
$$H_2CO_3 \rightleftarrows HCO_3^- + H^+ \quad (pKa_2 = 6.4) \quad (3)$$
$$CO_2(aq) + H_2O \rightleftarrows H_2CO_3 \quad (K = 2.8 \times 10^{-3}) \quad (4)$$

In the previous study, Fujiwara et al reported that desorption of CO_2 gas from low-concentration MEA solution (0.2 M) at low temperature (25 °C) using deaerating action of ultrasound.[2] Deaerating action of ultrasound can desorb CO_2(aq) which exists as a gas in a solution. However, it is difficult to desorb CO_2 gas from the other chemical species such as $RNHCOO^-$, HCO_3^-, and CO_3^{2-}. Therefore, ultrasound treatment is difficult to desorb CO_2 over pH 8.2 (**Fig. 1**).

Recently, Kojima et al reported that CO_2 is able to be desorbed from MEA solution by the synthesis of $CaCO_3$ using calcium chloride ($CaCl_2$).[3] The synthesis reaction of $CaCO_3$ is shown in Eq. (5).

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \quad (5)$$

In addition, the equilibrium of CO_2 in a solution can shift in the direction of the increase of CO_2(aq) due to the increase of H^+ concentration in a MEA solution by the synthesis reaction of calcium carbonate as shown in Eq. (5). Increasing of H^+ concentration increase concentration of CO_2(aq) from HCO_3^-. ($HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2(aq) + H_2O$). Fujiwara focused on the decrease of pH by the generation of $CaCO_3$ and reported the desorption of CO_2 gas from CO_2 dissolved MEA solution using ultrasound irradiation and $CaCl_2$ addition.[2] The desorption amount of CO_2 gas by the addition of $CaCl_2$ became higher than that of CO_2 gas without the addition of $CaCl_2$. In this study, we further investigated the enhancement of CO_2 gas desorption amount by the addition of $CaCl_2$ into the MEA solution. We also investigated the effect of the pH of MEA-CO_2 solution, $CaCl_2$ additive amount, and treatment time on the generation amount of $CaCO_3$ and desorption amount of CO_2 gas.

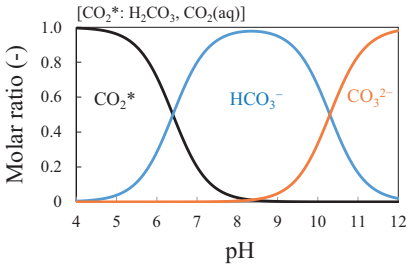

Fig. 1 Relationship between chemical speciation of CO_2 and pH in aqueous solution at 25 °C.

2. Experiment

CO_2-absorbed MEA solution (MEA-CO_2) was prepared by press-fitting of 0.5 MPa CO_2 gas for 60 min (purity >99.99%) through stirring (750 rpm) in a pressure-resistant container. The temperature of MEA solution during the press-fitting has a range of 20–25 °C because of the exothermic reaction between MEA and CO_2. The absorption amount of CO_2 in MEA solution was calculated from the increment amount of weight of MEA solution before and after CO_2 absorption. Desorption experiment of CO_2 gas from MEA

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solution was investigated using an ultrasonic generator (Kaijo, TA-4021) and 28 kHz-submersible transducers (Kaijo). In this paper, we confirmed the desorption amount of CO_2 gas from MEA solution using ultrasound irradiation with $CaCl_2$ addition of different Ca concentration. The transducer was placed at the bottom of a tank filled with water (15 °C). A flat-bottom flask containing the MEA-CO_2 solution (30 mL) was placed directly above the transducer. And then, $CaCl_2$ solution (30 mL) was added to the MEA-CO_2 solution (30 mL). Ca/CO_2 molar ratios in the mixed solution (60 mL) were set at 0, 0.05, and 0.5, respectively. Ultrasound was indirectly irradiated to the bottom of the flask through the water in a tank for 40 min. The ultrasound power was 11.8 W which value was calculated by the calorimetric method. The initial temperature of the mixed solution before ultrasound irradiation was set at 20 °C. The range of solution temperature during ultrasound irradiation was 20–25 °C by the increase of solution temperature due to the ultrasound energy reached. The CO_2 amount desorbed from MEA solution was evaluated from the weight loss of the solution and the generation amount of $CaCO_3$.

3. Results and discussion

MEA solution, which is mixture of MEA and ion-exchanged water, shows alkaline because OH^- is released as shown in Eq. (6). When CO_2 is injected into the solution, pH of the MEA solution decreased by consumption of OH^- in Eq. (7)–(9).

$$RNH_2 + H_2O \rightarrow RNH_3^+ + OH^- \quad (6)$$
$$RNH_3^+ + 2OH^- + CO_2 \rightarrow RNHCOO^- + 2H_2O \quad (7)$$
$$RNH_2 + CO_2 \rightarrow RNH_2^+COO^- \quad (8)$$
$$RNH_2^+COO^- + OH^- \rightarrow RNHCOO^- + H_2O \quad (9)$$

CO_2 absorption for MEA solution reaches equilibration at 20 min. Before, CO_2 desorption experiment, MEA-CO_2 solution was left for 90 min under ambient pressure to desorb CO_2 which is naturally released from MEA solution. The CO_2 absorption amount in MEA solution was 171 mM and the solution pH was 6.7. First, CO_2 desorption experiment from MEA solution using ultrasound without the addition of $CaCl_2$ was conducted. **Fig. 2** shows the changes of CO_2 desorption ratio and the pH values of MEA solution using ultrasound irradiation at each elapsed time. CO_2 desorption ratio and pH were increased with irradiation time. CO_2 desorption ratio was 37% and the pH rose from pH 6.7 to 8.2 at 30 min of sonication time. At the sonication of over 30 min, however, CO_2 desorption ratio and pH were approximately constant. The amount of CO_2(aq), which can be desorbed by ultrasound, is little at pH 8.2 (Fig. 1).

Next is the CO_2 desorption experiment from MEA solution using ultrasound irradiation with the addition of $CaCl_2$ to increase CO_2 gas desorption ratio. **Fig. 3** shows the molar balance of CO_2 after treatment of the MEA-CO_2 solution for 40 min using ultrasound with and without addition of $CaCl_2$. CO_2 desorption ratio and solution pH in the Ca/CO_2 molar ratio of 0, 0.05, and 0.5 were 37%, 43%, and 55%, and 8.2, 8.1, and 6.7, respectively. Desorption ratio of CO_2 gas indicated over 50% at 0.5 of Ca/CO_2 molar ratio. The pH of MEA solution decreased with the emission of H^+ by the synthesis reaction of calcium carbonate in a solution of Eq. (5). At the condition of $CaCl_2$ addition, the desorption amount of CO_2 gas was enhanced. We considered the reason the equilibrium shift of dissolved CO_2 as follows: $HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2(aq) + H_2O$. Total CO_2 desorption ratios containing $CaCO_3$ at the Ca/CO_2 molar ratio of 0.05 and 0.5 were 47% and 93%, respectively. In a presentation, we will make a presentation about the effect of pH and treatment time of MEA-CO_2 solution on the generation amount of $CaCO_3$ and desorption amount of CO_2 gas, respectively.

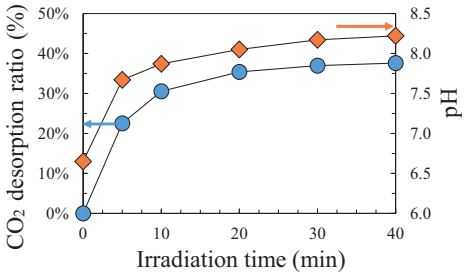

Fig. 2 Changes in CO_2 desorption ratio and the pH of MEA solution by ultrasound irradiation.

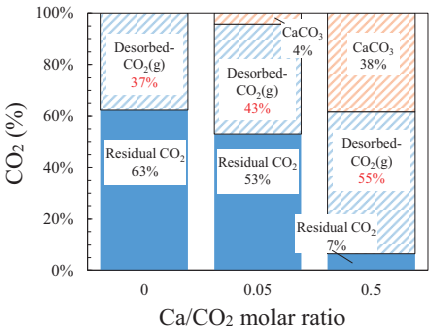

Fig. 3 Molar balances of CO_2 after treatment of the MEA-CO_2 solution for 40 min using ultrasound with and without addition of $CaCl_2$.

References

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