Hydration structure around CO_2 captured in aqueous amine solutions observed by high energy X-ray scattering

Carbon dioxide is widely recognized as a major greenhouse gas that causes the global warming problem. One approach to reducing CO_2 emission is CO_2 capture at thermal plants. Among various technologies for CO_2 capture, the chemical absorption method [1] using aqueous amine solutions is the closest to commercialization for large-scale plants.

The chemical absorption method is based on a reversible chemical reaction between CO_2 and an aqueous amine solution. CO_2 in flue gas is separated into the solution by contact with the CO_2-lean solution. After absorption, CO_2 is released from the CO_2-rich solution by heating. Then, the regenerated solution is used again in the absorption process.

Although some chemical absorption plants for factory-scale CO_2 emission sources have been under commercial operation, plants for large-scale CO_2 emission sources such as thermal plants are still under development. One significant way to improve chemical absorption is to develop a more efficient solution to be realized by such characteristics as high absorption capacity, a high absorption rate and a small thermal energy for regeneration. These properties depend on the hydration structure of chemical species bound with CO_2. Better understanding of the structure can bring a new insight into the improvement of the solution performance. However, the analysis of the hydration structure has some difficulties because the materials for the analysis are liquid systems.

We have been applying the high energy X-ray scattering method using SPring-8 to the analysis of the hydration structure and conformation of amine molecules [2-4]. Compared with spectroscopic methods, the X-ray scattering method has an advantage of the capacity to derive molecular structure directly through a distribution function. In this report, we describe the results obtained using 30 wt% monoethanolamine (MEA) aqueous solution before and after CO_2 absorption. MEA is a primary amine expressed in the chemical formula of $NH_2CH_2CH_2OH$, and is a typical and fundamental amine used for the chemical absorption method.

Measurements were carried out at the undulator beamline **BL16XU**. The incident X-ray wavelength was 0.3356 Å (36.94 keV). The scattered X-ray intensity from the sample solution was measured over a 2θ range of $0.5 \le 2\theta \le 80°$. The molar fractions of the sample solutions before and after CO_2 absorption were $(MEA)_{0.112}(H_2O)_{0.888}(CO_2)_x$ ($x = 0$ and 0.058, respectively). The sample solution was sealed in a flat plate acrylate resin cell with a thickness of 2 mm, which had X-ray transmission windows, each made of a Kapton film with a thickness of 25 μm. An empty cell was also measured for background intensity correction. The total exposure time was about 4–5 h for each sample solution.

Figure 1 shows the observed distribution function $g(r)$ of the sample solutions. In Fig. 1, the distribution function of a water sample is also shown for comparison. Three dominant peaks at $r = 1.0$, 1.5, and 2.8 Å are observed in $g(r)$ for the amine solution samples. The peak at $r = 1.0$ Å can mainly be ascribed to the intramolecular interaction of O–H within the water molecule. The peak at $r = 1.5$ Å is attributed to intramolecular interactions (mainly C–C, C–N, and C–O) in the amine (carbamate) molecule. The peak at $r = 2.8$ Å can be attributed mainly to the intermolecular hydrogen−bonded O···O interaction between the nearest neighbor water molecules. This peak also involves hydrogen−bonded O···O and N···O interactions concerning the nearest neighbor intermolecular amine···amine and amine···water interactions. Thus, atom pairs of the molecules existing in the sample solutions are clearly observed.

However, variations before and after CO_2 absorption are not clear. In order to clarify structural information on the captured CO_2, we derived a difference distribution function between before and after CO_2 absorption, $\Delta g_{CO_2}(r)$, as shown in Fig. 2. Peaks at $r = 1.2$ Å and 2.2 Å are obviously observed in the difference distribution function. These peaks
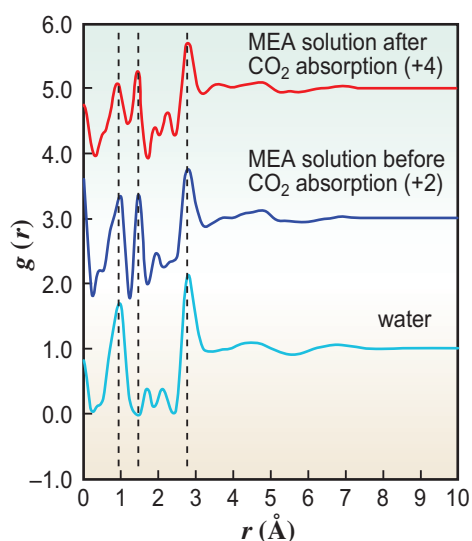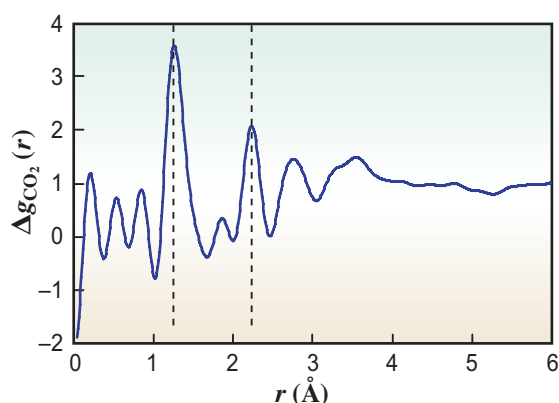

Fig. 1. Observed distribution functions.

Fig. 2. Difference distribution function observed between before and after CO_2 absorption.

are mainly attributed to the intramolecular C−O and nonbonding O···O interactions of captured CO_2, respectively.

The difference distribution function in Fig. 2 involves both intramolecular interactions within molecules that bind the captured CO_2 and intermolecular interactions between the captured CO_2 and its neighboring molecules. By subtracting the intramolecular contributions from the total distribution function, the intermolecular distribution function can be obtained. An NMR analysis showed that absorbed CO_2 molecules in the sample exist as MEA carbamate of 86 mol%, HCO_3^- /CO_3^{2-} of 13 mol%, and MEA carbonate of 1 mol%. The molecular structure of MEA carbamate was calculated theoretically using DFT calculation. Five stable carbamate structures were obtained. Although the
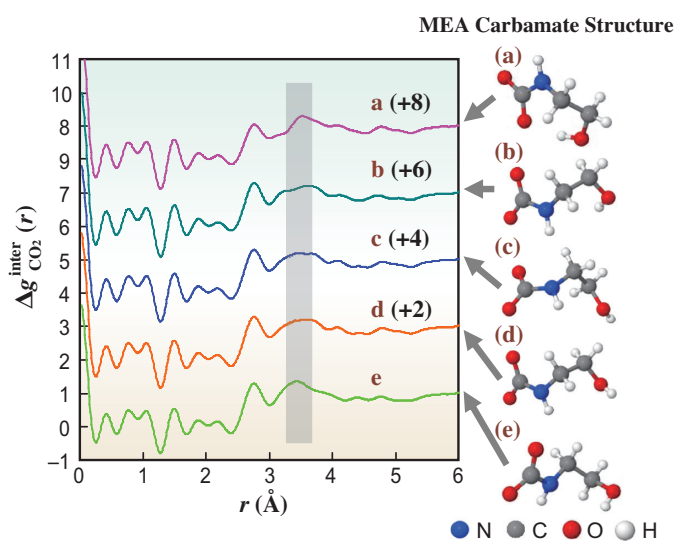
molar ratio between HCO_3^- and CO_3^{2-} is unknown, we considered the HCO_3^- molecule only and used the structure in a single crystal of $NaHCO_3$. The amine carbonate molecule was ignored because of its low molar ratio. From these molecular structures, we calculated the intramolecular interactions. By subtracting the intramolecular interactions from the total interactions, we obtained the intermolecular distribution function, $\Delta g_{CO_2}^{inter}(r)$, as shown in Fig. 3. The distribution functions in Fig. 3(a−e) were derived from the MEA carbamate structures (a)−(e), respectively. On the basis of any MEA carbamate structure, a broad peak at around $r = 0.35$ nm can be observed. By the detailed analysis, it was revealed that this peak originated from water molecules that formed hydrogen bonds with the captured CO_2. This result suggests that new hydrogen bonds are formed between the captured CO_2 molecules and the neighboring water molecules. Further study on other amine solutions showed that CO_2 captured as either amine carbamate or HCO_3^-/CO_3^{2-} formed hydrogen bonds with water molecules. Understanding of the hydrated structure at the molecular level will contribute to the development of new absorbing solutions with higher performance.

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Fig. 3. Intermolecular distribution functions around captured CO_2. The distribution functions a−e were derived from the MEA carbamate structures (a)−(e), respectively.

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