

## Enclathration of CO<sub>2</sub> as a Co-guest in sH Hydrates Formed from the CO<sub>2</sub> + N<sub>2</sub> + Methylcyclopentane Mixtures

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Among the well-known three types of gas hydrates, structure H (sH) hydrates have several noteworthy features compared to structure I (sI) and structure II (sII) hydrates. sH hydrates can capture large-sized liquid hydrocarbon guests in the presence of help gases such as CH<sub>4</sub> and N<sub>2</sub>. sH hydrates have a higher gas storage potential in their smaller cages compared to sI and sII hydrates, but the function of CO<sub>2</sub> as a co-guest molecule in sH hydrate has been still controversial. In order to investigate the enclathration of CO<sub>2</sub> as a co-guest in sH hydrates, the four-phase equilibria of the CO<sub>2</sub> + N<sub>2</sub> + methylcyclopentane (MCP) + water mixtures were measured and compared with three-phase equilibria of the corresponding CO<sub>2</sub> + N<sub>2</sub> + water mixtures. Furthermore, the structural transition according to the compositions of the gas mixtures (10, 20, 40, 60, and 80% CO<sub>2</sub>) was verified using Raman spectroscopy and powder X-ray diffraction (PXRD). At lower CO<sub>2</sub> concentrations, CO<sub>2</sub> was found to function as a co-guest of sH hydrates and due to the enclathration of MCP, four-phase equilibria showed a slight thermodynamic promotion. The structural transition from sH to sI was observed at CO<sub>2</sub> concentrations higher than 20%.