CHARACTERIZATION OF ALCOHOL+METHANE HYDRATE USING RAMAN SPECTROSCOPY AND X-RAY DIFFRACTION

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ABSTRACT
Hydrophilic substances are usually known to inhibit hydrate formation by thermodynamically altering the phase boundary for hydrate equilibrium to conditions of lower temperature and/or higher pressure. On the other hand, it has been reported that hydrophilic lower alcohols (ethanol, 1-propanol, and 2-propanol) form structure II hydrates with methane. However, the molecular level analysis of the role of alcohols in hydrate forming systems as guests based on the spectroscopic measurements has not been conducted. In the present study, we will elucidate enclathration of alcohol molecules using Raman spectroscopic measurements. The spectra of C-H stretching region of the alcohol molecules were measured before and after decomposition of the hydrate. Decomposition of the hydrate was detected by comparing the peak intensity of C-D and O-D stretching modes, which reflects the ratio of CD4 and D2O molecules in the hydrate sample. On the basis of comparison of the spectra of C-H stretching region collected before and after decomposition of the hydrate, the environmental change of the alcohol molecules upon the decomposition, which supports the simultaneous enclathration of CD4 and alcohol molecules, was observed. The results also suggest that the alcohol molecules show vapor-like behavior following the isolation of molecules with enclathration in the hydrate structure. In addition, in the system containing 2-propanol, simple 2-propanol hydrate formation was observed upon decomposition of the 2-propanol + methane hydrate. Structure II hydrate formation in all systems were confirmed with powder x-ray diffraction.

Keywords: alcohol hydrates, methane, ethanol, 1-propanol, 2-propanol, Raman spectroscopy

NOMENCLATURE

\( p \) pressure [MPa]
\( T \) temperature [K]
\( t \) time [min]

INTRODUCTION

Clathrate hydrates (or simply hydrates) are crystalline solid compounds composed of host water molecules and guest molecules.\[^{1,2}\] The water molecules form polyhedral cage structures while the guest molecules occupy the cages. A hydrate is thermodynamically stable at temperatures lower