Structure identification of binary 1-propanol+methane hydrate using neutron powder diffraction

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Abstract−Alcohols are frequently used in hydrate communities as thermodynamic hydrate inhibitors, but some alcohol molecules are also known to be hydrate formers with a help gas. In this study, the crystal structures of binary 1-propanol+methane hydrates at various temperatures were identified using neutron powder diffraction analysis with Rietveld refinement. Characteristic behaviors of the guest molecules in the hydrate structure were also analyzed to verify possible host-guest interactions from the refinement results. The results showed that the thermal factors of host water and guest methane increased continuously as the temperature increased. However, the isotropic thermal factors (B values) of 1-propanol were abnormally high compared to those of methane in the small cages of structure II (sII) hydrates, which could be because the 1-propanol molecules were off-centered in the large cages of sII hydrates. This implies that hydrogen bonding interactions between host and guest molecules can occur in the large cages of sII hydrates. The present findings may lead to a better understanding of the nature of guest-host interactions that occur in alcohol hydrates.

Keywords: Clathrate Hydrate, Neutron Powder Diffraction, 1-Propanol, Hydrogen Bonding

INTRODUCTION

Clathrate hydrates are non-stoichiometric crystalline compounds formed from 'host' water frameworks and 'guest' molecules [1-5]. Normally, 'canonical' clathrate hydrates refer to inclusion compounds of host-guest systems stabilized by van der Waals interactions between only the host and guest [1-5]. Several types of gaseous guest molecules can be selectively fitted into the hydrate cages; thus, clathrate hydrates can be considered as a future energy option for sustainable developments for energy and the environment [2,3]. For hydrate applications in these fields, the determination of hydrate phase equilibrium conditions is regarded as the key issue because clathrate hydrates can form under low-temperature and high-pressure conditions [1-5]. In addition, the measurement of the hydrate phase equilibrium point using the conventional isochoric method involves a time-consuming experiment for the determination of the intersection point of the cooling and heating curves in the pressure and temperature trace data [2,6]. Therefore, thermodynamic models based on the van der Waals-Platteeuw statistical theory have been applied to describe the hydrate equilibrium conditions [7]. The van der Waals-Platteeuw theory can be regarded as a very accurate model for the determination of the hydrate phase equilibrium conditions

as well as the effect of guest molecules in the hydrate cages, but the van der Waals-Platteeuw equation does not apply to recent findings about host-guest hydrogen bonding interactions [8-11].

Recent studies have reported that alcohols, which are frequently used as thermodynamic hydrate inhibitors in hydrate communities, can be enclathrated into the large cages of structure II (sII) or structure H (sH) hydrates [12,13]. Spectroscopic investigations confirmed that some alcohol molecules, such as 1-propanol, 2-propanol, *iso*-butanol, *tert*-butyl alcohol, 3-methyl-2-butanol, and 2-methyl-2-butanol, are hydrate formers that are enclathrated in the large cages of sII or sH hydrates without host-guest hydrogen bonding interactions, while 1-butanol and 3-methyl-1-butanol can be captured in the large cages of sII hydrates through possible host-guest hydrogen bonding interactions or the incorporation of the hydroxyl group of the alcohol molecules [13]. Youn et al. [14] have reported the effects of the position of the hydroxyl group in clathrate hydrate systems on hydrate stability. Lim et al. [15] investigated the effects of possible host-guest hydrogen bonding on hydrate phase equilibria using three diazine isomers, namely pyrazine, pyrimidine, and pyridazine, and the results showed that the hydrate phase equilibrium conditions can be shifted to higher pressures and lower temperatures as the host-guest hydrogen bonding interaction behaviors become stronger. To characterize the host-guest hydrogen bonding, Alavi et al. [8,10] conducted molecular dynamics simulations. Although the free OH signals of 1-propanol and 2-propanol encaged in the large cages of sII hydrates were observed in Raman spectra,

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indicating the presence of propanols that were not hydrogen bonded with cage water, Alavi et al. showed that long-lived (~10 ps) host-guest hydrogen bonding can still occur in the hydrates of propanols [8,10]. In addition, Udachin et al. investigated the possible guest-host hydrogen bonding interactions of alcohol hydrates via single-crystal X-ray diffraction [9].

We report here the structural identification of binary 1-propanol+methane clathrate hydrate using Rietveld refinement analysis of neutron powder diffraction (NPD) patterns. Characteristic behaviors of the guest molecules in the hydrate structure were also analyzed to verify the possible host-guest interaction from the refinement results.

EXPERIMENTAL DETAILS

1-Propanol-d$_8$ (C$_3$D$_7$OD, 98 atom% D) was purchased from Sigma Aldrich. Methane (CD$_4$) gas was supplied by Cambridge Isotope. Deuterated water (D$_2$O, 99.9 atom% D) was also purchased from Sigma Aldrich and used to minimize the incoherent scattering of hydrogen during NPD measurements. An alcohol solution (5.6 mol%, the stoichiometric amount for sII hydrates) was stored at 203 K for one day, and then it was ground into finely powdered samples with a 50 μm sieve under liquid nitrogen. The powdered sample was placed in a reactor with an inner volume of 15 mL, and then the reactor was pressurized with methane gas at up to 50 bar. The reactor was stored at 203 K for one week. The hydrate sample was ground again in liquid nitrogen and used for NPD measurements. The NPD experiments were performed using a high-resolution powder diffractometer (wavelength of 1.834333 Å) installed at 'HANARO' of the Korea Atomic Energy Institute (KAERI). The NPD patterns were refined using the Rietveld method with the FULLPORF program [16]. In the analysis, guest molecules

Fig. 1. Neutron powder diffraction patterns of the binary 1-propanol+methane clathrate hydrate in the 30-210 K temperature range.

Table 1. Atomic coordinates and isotropic factors of the binary 1-propanol+methane clathrate hydrate

Atom/molecule	x	Y	z
Oa	0.12500	0.12500	0.12500
Ob	0.21688	0.21688	0.21688
Oc	0.18298	0.18298	0.37309
Da	0.18329	0.18329	0.18329
Db	0.15813	0.15813	0.15813
Dc	0.20658	0.20658	0.27469
Dd	0.19644	0.19644	0.31717
De	0.14079	0.14079	0.37707
Df	0.22976	0.16065	0.39416
1-Propanol	0.37500	0.37500	0.37500
Methane	0.00000	0.00000	0.00000

were assumed to be a rigid body with identical isotropic thermal factors for all atoms. The centers of mass of 1-propanol and methane were fixed to the centers of cages (5^{12}6^4 cage for 1-propanol, 5^{12} cage for methane) with arbitrary rotation. The site occupancies of all host and guest atoms were fixed during refinement.

RESULTS AND DISCUSSION

Fig. 1 shows the NPD patterns of the binary 1-propanol+methane clathrate hydrate in the 30-210 K temperature range. In previous studies, the crystal structure of this binary clathrate hydrate was identified to be a cubic *Fd-3m* structure (sII hydrate) with a lattice parameter of ~17.2 Å, and our NPD patterns were consistent with literature results [2,3,9,13]. The atomic coordinates calculated from the Rietveld refinement results are shown in Table 1.

The main diffraction peaks were from the binary 1-propanol+methane clathrate hydrate, but we also observed evidence of a small amount of hexagonal ice (I*h*) phase and aluminum from the NPD sample holder in Figs. 1 and 2. Figs. 2(a) and 2(b) show the refined NPD patterns of the binary 1-propanol+methane clathrate hydrate collected at 30 and 150 K. The red circles indicate the observed NPD profile of this binary clathrate hydrate, the black solid line shows the calculated NPD profile, and the lower blue solid line represents the difference profile between the observed and calculated profiles. The blue, red, and green tick marks show the reflection positions of sII hydrate, hexagonal ice, and aluminum from the sample holder, respectively. The lattice parameters of sII hydrate in the 30-210 K temperature range are shown in Fig. 3, while reasonable reliability factors are shown in Table 2. The lattice parameter of the binary 1-propanol+methane clathrate hydrate increased continuously as a function of temperature. The thermal expansion coefficients of these binary clathrate hydrates have also been determined in previous studies [17,18]. Fig. 4(a) shows the normalized lattice parameters of the binary 1-propanol+methane clathrate hydrate in the 30-210 K temperature range. The thermal expansion trend of our sII clathrate hydrate was similar to the literature trend [17,18], and thus, we could not find a significant difference between the thermal expansion coefficient of the binary 1-propanol+methane clathrate hydrate, shown in Fig. 4(b), and the
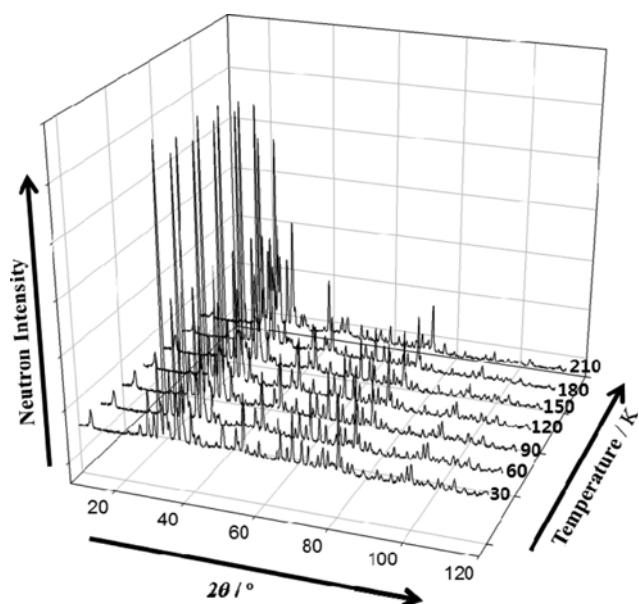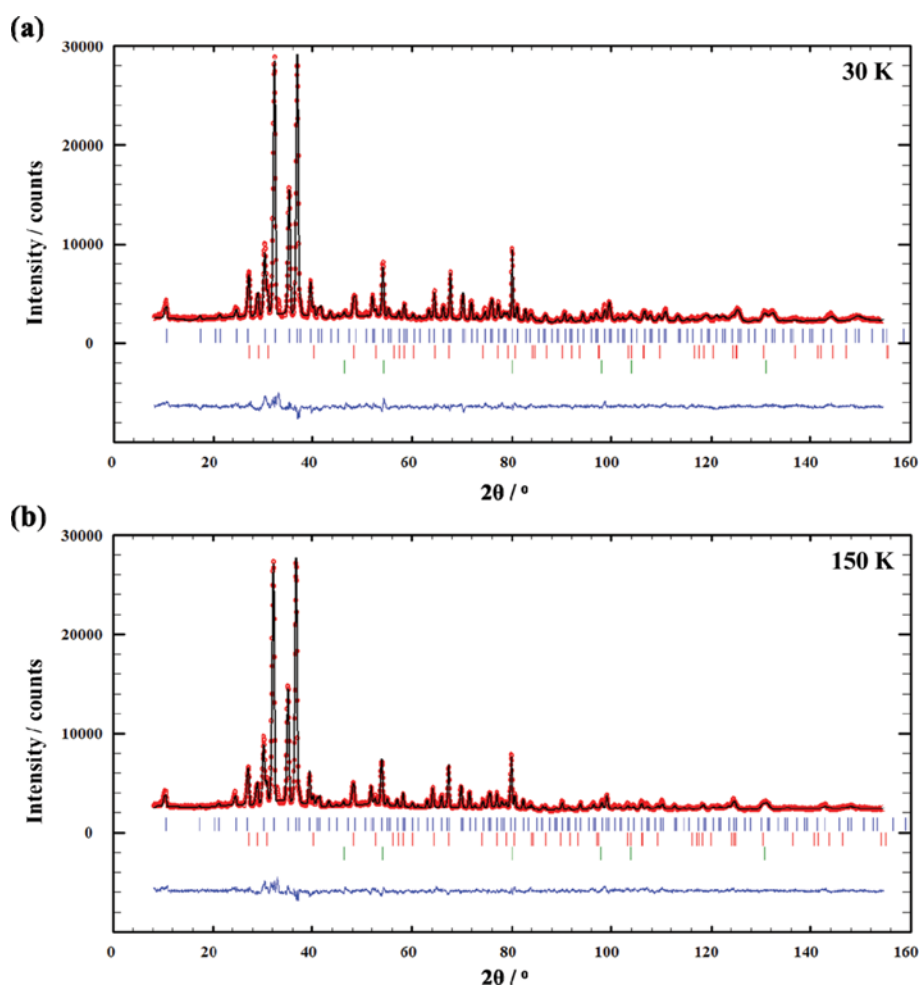
Fig. 2. Refined NPD patterns of the binary 1-propanol+methane clathrate hydrate collected at 30 and 150 K.

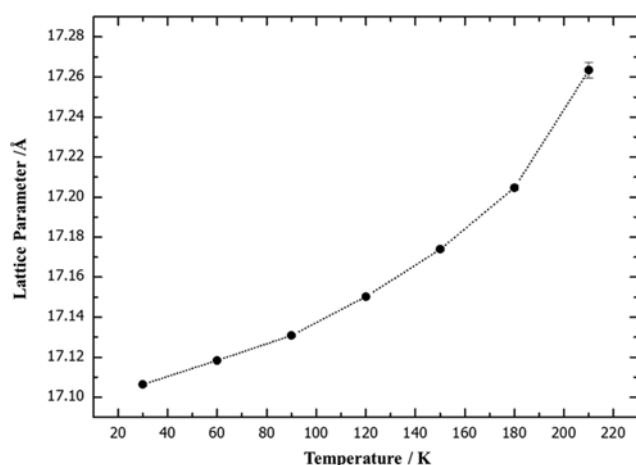**Fig. 3. Lattice parameters of the binary 1-propanol+methane clathrate hydrate.**

Table 2. Reliability factors for the refinements for the binary 1-propanol+methane hydrate

Temperature (K)	χ^2	R_{wp} (background subtracted)
30	7.28	15.1
60	6.88	14.9
90	6.75	15
120	6.49	15
150	6.11	14.9

literature value [17,18].

To determine the characteristic behaviors of alcohol molecules in hydrate cages, we focused on the thermal factors of the host and guest from NPD analysis. Figs. 5, 6, and 7 show the isotropic thermal factors (B values) of the guest molecules (methane), host oxygen, and host hydrogen, respectively. Except for O_f, as shown in Fig. 6, all of the thermal factors (B values) showed a continuous increase as temperature increased. The lattice parameter of the binary 1-propanol+methane clathrate hydrate increases as a function of temperature; therefore, the B values can be attributed to thermal expansion behaviors. In addition, the B values of all host hydrogen atoms also increased as the temperature increased, except for D_a (Fig. 7).

An interesting feature could be observed in the guest molecules. As described in the Experimental section, we assumed that the guest molecules were rigid bodies and were located at the cen-
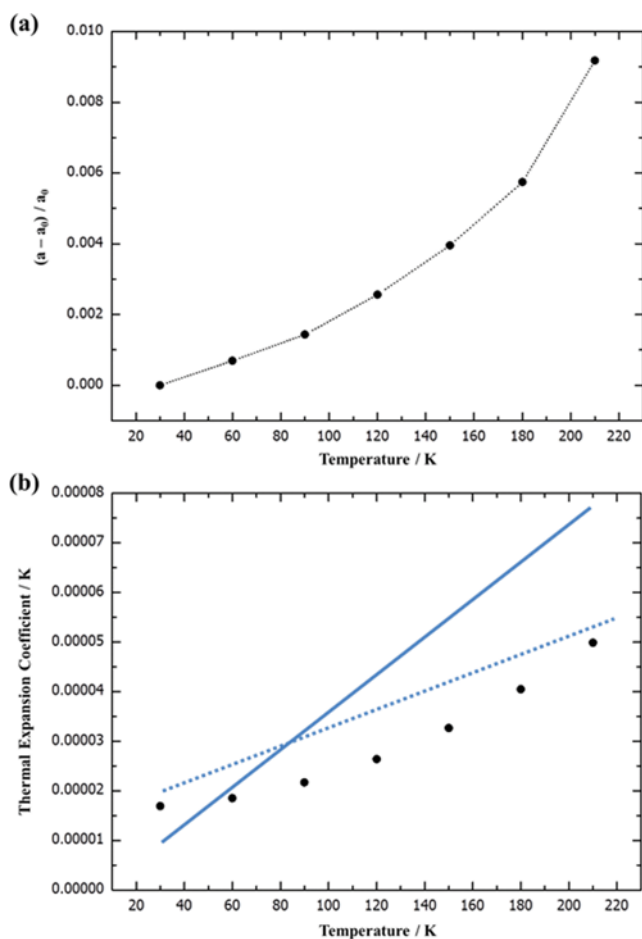
Fig. 4. (a) Normalized lattice parameters and (b) thermal expansion coefficients of the binary 1-propanol+methane clathrate hydrate. Solid line shows the thermal expansion coefficients of sI hydrates, and dashed line indicates the thermal expansion coefficients of sII hydrates.
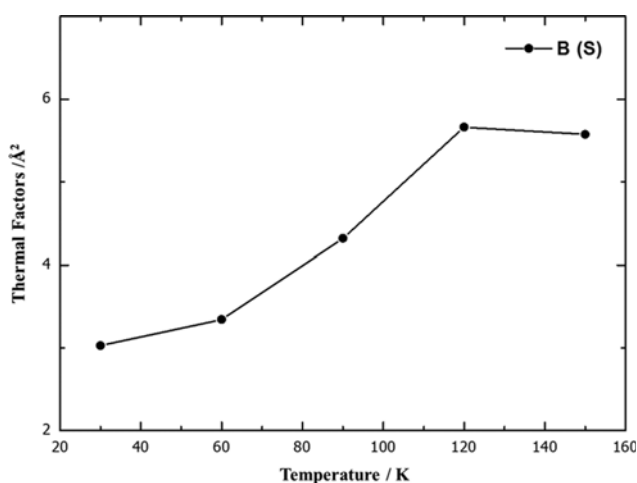

Fig. 5. Isotropic thermal factors of guest molecules in the small cages of sII hydrate.

ter of the cages with arbitrary rotation for the refinement analysis. In Fig. 5, the B values of methane in the small cages of sII hydrates
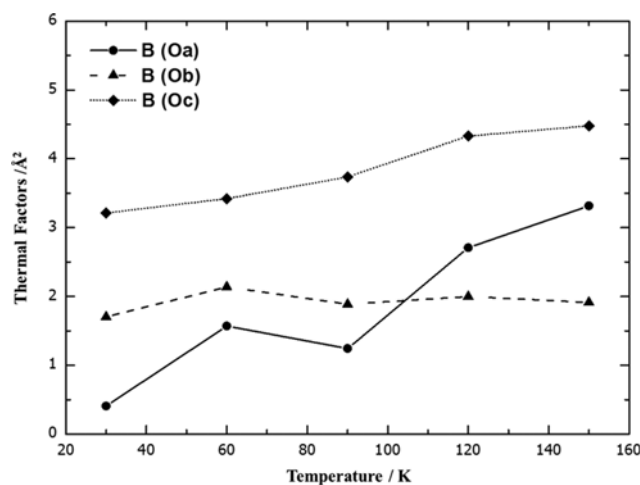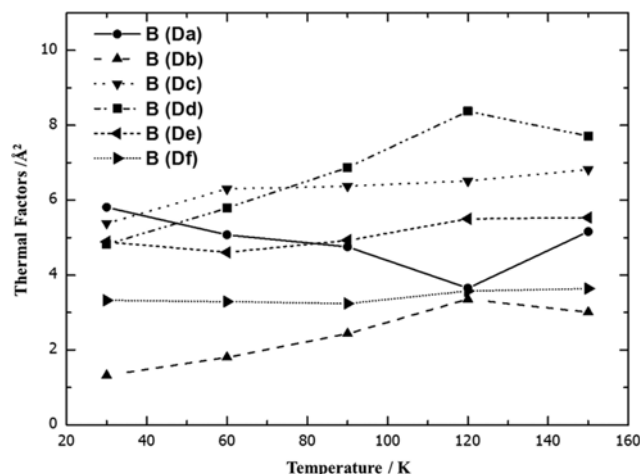

Fig. 6. Isotropic thermal factors of host oxygen atoms.

Fig. 7. Isotropic thermal factors of host deuterium atoms.

rises as temperature increases. The continuous increase of the B values for methane in the small cages shown in Fig. 5 is reasonable and implies that methane is not significantly off-centered. On the other hand, the B values of 1-propanol are abnormally high compared to those of methane in the small cages. This might be because the atomic coordinates of the guest molecules were at the centers of the cages for the structural analysis while 1-propanol is actually largely off-centered as a result of hydrogen bonding with cage water molecules; thus, further analysis of the B values for 1-propanol was excluded in this study. Although we have reported that free OH signals of 1-propanol encaged in the large cages of sII hydrates are observed in Raman spectra [13], indicating the presence of 1-propanol that was not hydrogen bonded with cage water, the findings of this study may reveal that hydrogen bonding interactions between host and guest can be possible. Alavi et al. [8] investigated the changes in the probability of hydrogen bonding between host and guest molecules with temperature, and the results showed that the probabilities of hydrogen bond formation for 1-propanol and 2-propanol decreased continuously as the temperature increased. With the decreases in the hydrogen-bonding prob-

abilities, the observation of free OH for 1-propanol molecules in the large cages of sII hydrate in Raman spectra may be possible [13].

CONCLUSION

We identified the crystal structures and determined the characteristic behavior of guest molecules for binary 1-propanol+methane hydrates at various temperatures through NPD studies. Rietveld refinement of the NPD data was performed to analyze the possible host-guest interactions. The results showed that the thermal factors of host water and methane molecules increased continuously as the temperature increased. However, the B values of 1-propanol were abnormally high compared to those of methane in the small cages of sII hydrate, and this could be because the 1-propanol molecules were off-centered in the large cages of sII hydrate. Therefore, this implies that hydrogen bonding interactions between host and guest molecules can occur in the large cages of sII hydrate.

ACKNOWLEDGEMENTS

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