

Molecular Behavior of 1-Pentanol Guest in the NH₄F-doped Clathrate Hydrate

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Abstract

In pure water, and, even in the presence of help gases, 1-pentanol (1-PeOH) does not form a clathrate hydrate structure. Its size is not appropriate for either the structure II 5¹²6⁴ or structure H 5¹²6⁸ cages and the presence of a hydrophilic OH group that tends to destabilize the clathrate hydrate framework through guest- host hydrogen bonding. Recently, the NH₄F doping of the clathrate framework was suggested to make the hydrate lattice more resistant to disruption by host-guest hydrogen bonding. In this study, we report the synthesis of 1-pentanol + methanol binary structure II clathrate hydrate doped with NH₄F and demonstrate that the space filling of 1-pentanol as a guest molecule can be managed by hydrogen bonding between doped NH₄F in the water framework and the hydroxyl group of 1-pentanol. The structural characterization of 1-PeOH + methanol hydrates was conducted by powder X-ray diffraction (PXRD) pattern analysis and solid state ¹³C NMR spectroscopy. The 1-PeOH guest

conformations and molecular interactions in the clathrate cages and the guest conformations were also investigated by solid state ^{13}C NMR spectroscopy and molecular dynamics simulations. Additionally, the 1-PeOH hydroxyl group was observed to be incorporated in the clathrate hydrate water framework. The findings in this work show that doping the clathrate hydrate lattice with NH_4F and using methanol as a helper guest can be used for stabilizing heavier alcohol molecules which cannot be engaged in normal clathrate hydrates.

Keywords

Clathrate Hydrate, Hydrogen Bonding, Ammonium Fluoride

1. Introduction

In clathrate hydrates, alcohol guest molecules have both a hydrophilic part which destabilizes the hydrogen bonded water cages and a hydrophobic part to stabilize the host framework. Many alcohols from C2 to C5 form sII or sH hydrates in the presence of helper gases such as methane or xenon [1-8]. For C5 amyl alcohols, there are eight isomers and it was reported that two of the isomers, 3-methyl-2-butanol and 2-methyl-2-butanol form sH hydrates with methane and that another two, 3-methyl-1-butanol and 2,2-dimethyl-1-propanol form sII hydrates with methane. Although the molecular sizes of 3-methyl-1-butanol and 2,2-dimethyl-1-propanol (based on the largest van der Waals radii) are quite a bit larger than the size considered suitable for the $5^{12}6^4$ cages [8,9], the guest-host hydrogen bonding between the OH of alcohols and host water molecules allows these large molecules to fit into the large cages of sII hydrates [8]. The other four isomers, 1-pentanol (1-PeOH), 2-pentanol, 3-pentanol, and 2-methyl-1-butanol cannot be engaged in the large cage of either sII or sH hydrate even in the presence of methane [8].

Recently, the NH_4F doping of the clathrate framework was suggested to make the hydrate lattice more resistant to disruption by host-guest hydrogen bonding [10,11]. It was demonstrated by powder X-ray diffraction (PXRD) analysis and ^2H and ^{13}C NMR spectroscopy that methanol forms not only simple sI clathrate hydrate but also binary clathrate hydrates of sII 1,2-propanediol + methanol and sH tert-butyl methyl ether + methanol systems when the guest-host hydrogen bonding is managed by NH_4F doped into the framework [10,11]. It was also reported that many large guest molecules such as ethanol, 3-methyl-1-butanol (isoamyl alcohol), and 2-methyl THF can form binary sI or sII methanol clathrates [11]. Although methanol is an ethane-sized molecule, in the presence of NH_4F , methanol is a good guest suitable for not only for the $5^{12}6^2$ cages in sI hydrate, but also for the smaller regular (5^{12}) and irregular ($4^35^66^3$) dodecahedra in sI, sII or sH hydrates. Thus, in the doped binary hydrate systems, methanol acts as a helper guest like methane or xenon for various alcohols to form clathrate structures.

In this study, we report the synthesis and the identification of 1-pentanol + methanol clathrate hydrate doped with NH_4F . Powder X-ray diffraction (PXRD), solid-state ^{13}C NMR spectroscopy, molecular dynamics (MD) simulation methods were applied to study the structure and conformation of 1-PeOH in a NH_4F doped hydrate.

2. Experimental

2.1. Sample Preparation

An aqueous solution of 27 mol% NH_4F was quenched drop by drop in liquid nitrogen. The frozen solution was ground to a fine powder and immersed in a cold mixture of 1-PeOH/methanol (1:2 molar ratio) for 5 days in dry ice. After this procedure, the residual liquid was absorbed into filtration paper, the solid sample was collected and kept in liquid nitrogen.

2.2. Powder X-ray Diffraction

The PXRD patterns of samples were recorded at 100 K on the supramolecular crystallography beamline (2D) at the Pohang Accelerator Laboratory (PAL) in Korea. An ADSC Quantum 210 CCD diffractometer with a synchrotron radiation of 0.9000 Å wavelength was used. The fine sample powder was placed in precooled polyimide tubing (Cole-Parmer, USA) and which was loaded into the diffractometer. Two-dimensional patterns of 4096 by 4096 pixels were recorded and converted into one-dimensional patterns of 2θ range from 0 to 66.9932° . The exposure time of the sample was below 30 s so as to minimize the sample damage by the synchrotron radiation.

The obtained patterns were refined by Rietveld refinement with the FULLPROF program [12]. The 1-PeOH and methanol guest molecules were assumed to be rigid bodies and inserted into the centers of cages with arbitrary rotations. We also assumed that the large $5^{12}6^4$ cages of sII hydrate phase were fully occupied by 1-PeOH. Because the atomic scattering factor of hydrogen is too small to use for refinement, we used virtual species with sums of atomic scattering factors for H_2O , $-\text{CH}_2-$, $-\text{CH}_3$, and $-\text{OH}$ by following the method reported in previous work [10,11,13]. Ammonium and fluoride ions are not distinguishable from water because of disorder and the similarity of their scattering factors, thus we assumed that there were only water molecules in the host sites.

2.3. NMR Spectroscopy

The ^{13}C solid-state high power ^1H -decoupled (HPDEC) and cross-polarized (CP) NMR spectra were obtained on a Bruker DSX 400 instrument (magnetic field of 9.4 T, ^{13}C Larmor frequency of 100.67 MHz). The sample powders were packed in 4 mm zirconia rotors in liquid nitrogen and the spectra were recorded with magic angle spinning (MAS) at 2.5 kHz at 200 K. The pulse repetition delay in the HPDEC experiments was set at 10 s. The downfield

carbon signal of adamantane was set to 38.56 ppm at 298 K and used as a chemical shift reference.

2.4. Molecular Dynamics Simulation

The MD simulations were performed with DL_POLY version 2.20 [14] using the leapfrog algorithm with a time step of 1 fs, a total simulation time of 1.1 ns with an equilibration time of 0.1 ns at 200 K and 1.013 bar in NPT ensemble [15-17]. The position of the water oxygen atoms of the sII clathrate hydrate from X-ray crystallography and the water hydrogen atom positions determined by Takeuchi et al. were used for the initial configuration of the hydrate framework [18]. One pair of adjacent water molecules for each of the eight large cages of the sII hydrate unit cell, were randomly chosen and replaced with eight ammonium fluoride pairs to replicate a doped hydrate phase. A $2 \times 2 \times 2$ replica of the unit cell was used with 64 large cages occupied by flexible 1-PeOH guests and 128 small cages occupied by CH₃OH. In the simulations, the van der Waals and electrostatic intermolecular interactions of water are modelled with the TIP4P/ice potential [19], ammonium with the force field of Boudon and Wipff [20], fluoride with the universal force field of Rappe et al. [21]. The van Leeuwen and Smit united atom force field was used for methanol [22] and the General AMBER force field (GAFF) was used for 1-PeOH [23]. The water, ammonium fluoride, and methanol guest molecules were given freedom of motion in the simulations but their internal structure was considered rigid, but the large guest molecules have flexible bond lengths, bond angles, and dihedral angles. A cutoff of 15 Å was used for the short-range potentials in the simulation.

3. Results and Discussion

As the first step, it was checked by the PXRD analysis whether 1-PeOH can indeed form a stable clathrate structure. 1-PeOH is a long chain molecule with a length approximating that of n-hexane and it was reported that n-pentane and n-hexane are not able to stabilize the sII or sH hydrates [24,25]. They may be too large to be encaged in the $5^{12}6^4$ cage of sII hydrate and may not fill the $5^{12}6^8$ cage of sH hydrate efficiently. Fig. 1 shows the PXRD pattern of the H₂O/NH₄F solid (27 mol% NH₄F) immersed in 1-PeOH/methanol (1:2 mole ratio) liquid and its refinement result from Rietveld analysis. As seen in Fig. 1, the pattern was well refined with agreeable reliability factors (background subtracted Rwp: 10.6% and χ^2 : 2.58) mainly by the cubic $F\bar{4}3m$ space group (lattice parameter: $a = 17.0721(10)$ Å) and some impurities of cubic $Pn\bar{3}n$ and hexagonal $P6_3/mmc$ phases. The $Pn\bar{3}n$ phase is from sI simple methanol clathrate doped with NH₄F as previously reported [10,11], and the $P6_3/mmc$ phase is from the unreacted H₂O/NH₄F solid solution. Therefore, the $F\bar{4}3m$ phase should be the sII binary 1-PeOH + methanol H₂O/NH₄F clathrate.

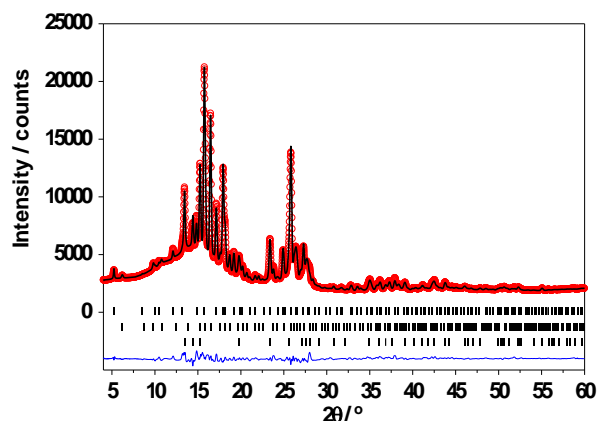


Fig. 1. The PXRD pattern of 1-PeOH + methanol H₂O/NH₄F clathrate refined by the Rietveld analysis. (Bragg ticks: $Fd\bar{3}m$ for the first row, $Pm\bar{3}n$ for the second row, and $P6_3/mmc$ for the third row). Adapted from Ref. 26 with permission from the Royal Society of Chemistry.

As the next step, we determined the conformers of liquid and encaged 1-PeOH from the ¹³C NMR spectra. Fig. 2 shows the CP ¹³C NMR spectra of 1-PeOH + methanol H₂O/NH₄F clathrate recorded at 200 K. For comparison, the HPDEC ¹³C NMR spectrum of liquid 1-PeOH in H₂O/NH₄F solid solution without methanol recorded at 220 K is also shown. If the C atoms in 1-PeOH are numbered from 1 for the C neighbored by O atom to 5 for the end C atom of the chain (O-C¹-C²-C³-C⁴-C⁵), either gauche- (G) or anti- (A) positions for 1-2, 2-3, and 3-4 carbon bonds of the heavy atom dihedral angles are determined, respectively. We can classify 8 types of 1-PeOH conformers, GAA, AAA, GGA, GAG, AAG, AGA, GGG, and AGG. The GGA, GAG, GGG, and AGG types have two or more possible conformers and there are 14 possible conformers for 1-PeOH molecule. All conformers were geometrically optimized by density functional theory (DFT) at the B3LYP/6-311++G(2d,p) level and ¹³C NMR isotropic chemical shielding for each optimized structure was calculated by the gauge invariant atomic orbital (GIAO) method at the B3LYP/6-311++G(2d,p) level [27] and the calculated chemical shifts of each conformer are tabulated in Table 1. From the comparison of the chemical shift of each carbon atom relative to C⁵, $\Delta\delta = \delta(C^x) - \delta(C^5)$ between the calculated and the experimentally observed chemical shifts for each conformer [28], it is concluded that the form of 1-PeOH in neat liquid is predominantly GGA1 (Fig. 2).

Since the 1-PeOH guest molecule in the clathrate cage is both strongly interacting with host water and NH₄F of the lattice and is also slightly distorted in the cage compared to the ideal forms of the isolated conformers, the direct comparison of $\Delta\delta$ between the calculated and the observed chemical shifts has some uncertainty for predicting the 1-PeOH conformation. However, we expect the relative order of chemical shifts for the carbons obtained from the calculations should still be an acceptable reference for the experimental values. As seen in Fig.

2, the chemical shifts of four carbons of 1-PeOH in the clathrate except C¹ are evidently shifted upfield. The C¹ is slightly deshielded in the clathrate. Among 14 conformers, only two conformers, GGG1 and AGG1, have more shielded C² - C⁵ than those of GGA1 (Fig. 2 and Table 1). Thus, we can consider these two conformers as candidates for the 1-PeOH guest in the cages.

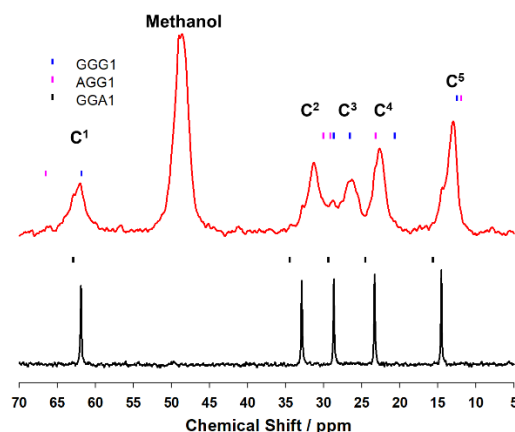


Fig. 2. The HPDEC ¹³C NMR spectrum of 1-PeOH in H₂O/NH₄F frozen solution (black) and the CP spectrum of 1-PeOH + methanol H₂O/NH₄F clathrate (red) with the ticks denoting the calculated chemical shifts (black: GGA1, pink: AGG1, blue: GGG1). Adapted from Ref. 26 with permission from the Royal Society of Chemistry.

Table 1

The predicted chemical shifts of fourteen optimized 1-PeOH conformers at the B3LYP/6-311++G(2d,p) level [26].

Energy Order	Conformer	Predicted Chemical Shifts (ppm)				
		C ¹	C ²	C ³	C ⁴	C ⁵
1	GAA	67.44	36.33	33.70	28.45	15.78
2	AAA	68.63	36.28	32.48	28.27	15.72
3	GGA1	62.90	34.43	29.36	24.54	15.63
4	GAG1	67.45	33.13	30.93	26.24	13.24
5	AAG	69.01	33.20	30.24	26.42	13.42
6	GAG2	67.63	33.22	31.64	26.68	13.45
7	AGA	67.56	34.71	32.85	26.80	15.95
8	GGA2	71.16	38.47	34.67	28.58	16.20
9	GGG1	61.78	28.66	26.55	20.66	12.47
10	AGG1	66.50	30.05	29.12	23.14	11.93
11	GGG2	70.79	36.22	29.53	24.93	12.84
12	GGG3	67.38	34.51	29.22	25.93	14.71
13	AGG2	68.58	37.53	30.76	27.54	17.34
14	GGG4	68.91	36.59	35.26	26.62	15.84

In order to check the preference between GGG1 and AGG1 in the $5^{12}6^4$ cages, we conducted MD simulations with rigid and geometrically optimized conformers in the large cages of the clathrate phase. Both rigid GGG1 and AGG1 stabilize the sII clathrate structure in the simulations. Two sample large cages with NH_4F doping which encapsulate 1-PeOH molecules are shown in Fig. 3(a) in the GGG1 conformation and Fig. 3(b) in the AGG1 conformation. Similar to the case of 3-methyl-1-butanol studied by Hiratsuka et al. [29], the $-\text{OH}$ group of 1-PeOH inserts in between water molecules of the clathrate hydrate framework and distortions of the cage structure on that side of the guest molecule. However, these distortions are randomly positioned in the sII clathrate lattice and do not lead to the dissociation of the structure. Methanol molecules in the adjacent small cages (Fig. 3(a)) help stabilize the distorted water framework by hydrogen bonding with the dangling hydrogen bonds of the water molecules of the framework near the $-\text{OH}$ group of 1-PeOH. The configurational energies (total potential energies) of these two systems were calculated as -16228 kJ per 1 mol unit cell for GGG1 and -16332 kJ per 1 mol unit cell for AGG1, respectively. Because there are eight 1-PeOHs in the unit cell, one mole of AGG1 conformer stabilizes a unit cell by as much as 13 kJ than the GGG1 conformer.

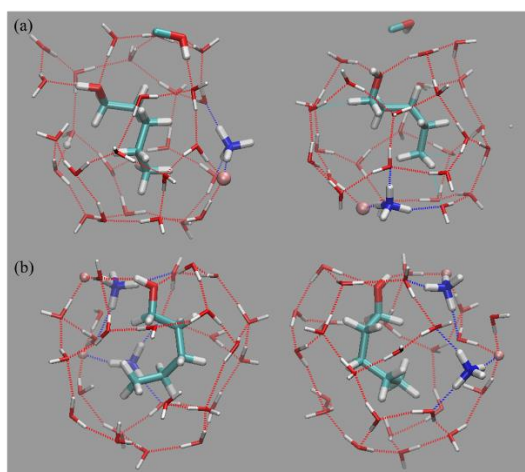


Fig 3. (a) Sample snapshots of rigid 1-PeOH molecules with the GGG1 conformations in two of the sII large cages extracted from the simulation trajectory. (b) Sample snapshots of rigid 1-PeOH molecules with the AGG1 conformations in the sII large cages extracted from the simulation trajectory. Adapted from Ref. 26 with permission from the Royal Society of Chemistry.

The MD simulation results above indicate that AGG1 is the most suitable conformer in the sII $\text{H}_2\text{O}/\text{NH}_4\text{F}$ clathrate. However, there are some differences between the simulation and experimental conditions. In the simulation, both AGG1 and GGG1 conformers were rigid but 1-PeOH in reality is not rigid but flexible, thus the molecular structures of AGG1 or GGG1 encapsulated in the cages in hydrate may not be the same as the rigid and optimized structure.

Additionally, in the simulation, only one pair of NH_4^+ and F^- were inserted per each $5^{12}6^4$ cage whereas 27 mol% NH_4F solution was used in this experiment which means that ~42% of host water positions are replaced by NH_4^+ or F^- . It is certain that there is a considerable number of NH_4F in the large cage, strongly interacting with 1-PeOH. The OH conformation is the only difference between AGG1 and GGG1, thus it is more reasonable to consider that the OH of 1-PeOH is freely rotatable in the cage by interacting with NH_4F and thus that there exist many intermediate structures between AGG1 and GGG1 in the NH_4F doped $5^{12}6^4$ cages.

4. Conclusion

In this study, we demonstrated that 1-PeOH is encaged in the $5^{12}6^4$ cages of sII $\text{H}_2\text{O}/\text{NH}_4\text{F}$ clathrate in the presence of methanol helper guest. The crystal structure of 1-PeOH + methanol clathrate was identified by PXRD analysis and the conformation of the 1-PeOH in the clathrate phase was determined by ^{13}C NMR spectroscopy with DFT calculations of the NMR chemical shifts of all possible conformers of 1-PeOH. In the simulations, the 1-PeOH hydroxyl group shows a preference for hydrogen bonding with the NH_4F dopant of the framework. The presence of dopant in the lattice framework tends to attract the hydrogen bonding of the guest molecules and to prevent the formation of guest-induced Bjerrum defects in the water lattice. According to this result, methanol can easily be incorporated in the clathrate cages of the doped phase. The findings in this work show that doping the clathrate hydrate lattice with NH_4F and using methanol as a helper guest can stabilize heavier alcohol molecules which cannot be encaged in normal clathrate hydrates.

The content presented in this Proceedings volume includes part of the published paper: *CrystEngComm*, 2021, **23**, 4708.

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