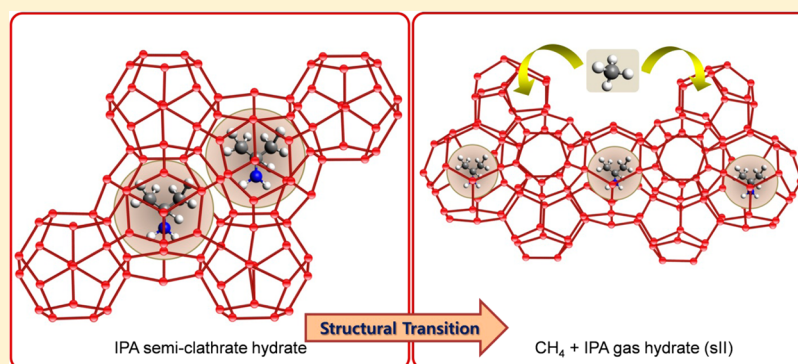# Structural Transformation of Isopropylamine Semiclathrate Hydrates in the Presence of Methane as a Coguest

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IPA semi-clathrate hydrate — Structural Transition → CH₄ + IPA gas hydrate (sII)

ABSTRACT: Guest-induced structural transformation in amine semiclathrate hydrates is a unique pattern caused by modifying the hydrophobic−hydrophilic balance, and thus, it can be applied to potential gas storage and transportation areas. The experimental results of the structural transformation of isopropylamine (IPA) semiclathrate hydrates in the presence of methane (CH_4) as a coguest are presented with a focus on the macroscopic phase behavior and microscopic analytical methods such as powder X-ray diffraction (PXRD) and NMR spectroscopy. The introduction of CH_4 molecules as coguests changed the structure of the IPA·$8.0H_2O$ semiclathrate hydrates (hexagonal, $P6_3/mmc$) to sII gas hydrates (cubic, $Fd3m$). The microscopic analysis results indicate that the guest gas distribution and the clathrate hydrate composition can be altered with adjustment of the IPA concentration. The overall experimental results are valuable for increased understanding of the stability conditions, structural details, and guest−host interactions in hydrophobic guest gas + IPA clathrate hydrates.

INTRODUCTION

The inclusion compounds formed by the accommodation of guest molecules into hydrogen-bonded water frameworks are called clathrate hydrates and they can be divided into true and semiclathrate hydrates.[1] True clathrate hydrates share many physical and chemical properties with semiclathrate hydrates because the primary component of both crystal structures is water molecules. The primary difference between these clathrate hydrates is that in true clathrate hydrates there are no direct chemical interactions between the host and guest molecules, while in semiclathrate hydrates some chemical compounds can act as both host and guest molecules simultaneously, and thus, the guest molecules can form hydrogen bonds with the water molecules or have ionic interactions with the host molecules to form the host framework.[1−5] However, recent investigations have indicated that chemical compounds with nitrogen or oxygen atoms in the functional group exhibit guest−host interactions such as hydrogen bonding due to their strong electronegativity, which results in the strict distinction between true and semiclathrate hydrates becoming blurred for some specific chemical compounds.[6,7]

The well-known gas hydrates belong to true clathrate hydrates and can form three different crystal structures of sI, sII and sH, which contain differently sized and shaped cages that primarily depend on the molecular sizes of guest species. Small-sized guest molecules such as CH_4 or CO_2 form sI hydrates, and much larger guest molecules such as C_3H_8 or THF form sII hydrates. In addition, large liquid hydrocarbon molecules such as neohexane or methylcyclohexane form sH hydrates in the presence of help gases.[1]

Some acids such as $HClO_4$ and HPF_6 and the bases or their analogues such as quaternary ammonium salts (QAS) form ionic semiclathrate hydrates.[2−5,8−10] In the tetra-n-butylammonium bromide (TBAB) or tetra-n-butylammonium fluoride (TBAF) semiclathrate hydrates that belong to the QAS semiclathrate hydrates, the anions form cage structures with water molecules, and the tetra-n-butylammonium cations occupy large partially broken cages that were formed after merging and distortion.[2−5] Meanwhile, many alkylamine

compounds have been known to form semiclathrate hydrates, except *tert*-butylamine, which forms true clathrate hydrates.[2] In alkylamine semiclathrate hydrates, the functional group of guest molecules forms hydrogen bonds with water molecules in order to construct the host framework, while the hydrophilic alkyl chain of guest molecules occupies the cages.[2]

The structural changes in the *tert*-butylamine hydrates, which are true clathrate hydrates, in the presence of coguests such as CH_4 and H_2 for application in gas storage have been investigated.[11−13] However, the guest-induced structural changes in alkylamine semiclathrate hydrates have rarely been examined or have been examined in very limited systems.[14,15] In particular, there have been no experimental results for the guest-induced structural changes in isopropylamine (IPA) semiclathrate hydrates whose structure is most closely related to the gas hydrates.[16] Therefore, in this study, systematic experimental approaches based on the macroscopic phase behavior and microscopic structural characteristics of IPA semiclathrate hydrates in the presence of CH_4 as a coguest are reported for their potential application to new gas storage materials.

The phase equilibria of the double CH_4 + IPA gas hydrates will be useful not only in estimating the formation/dissociation conditions and stability regions but also in designing a gas storage process. In addition, the microscopic analysis will provide valuable information about the structural transition and guest distribution in the double CH_4 + IPA gas hydrates. Therefore, the three-phase equilibria [clathrate hydrate (H)−liquid water (L_W)−vapor (V)] for the ternary CH_4 + IPA + water mixtures at three different IPA concentrations (1.0, 5.6, and 11.1 mol %) were measured. The structural changes due to the introduction of CH_4 as a coguest were analyzed using microscopic methods such as NMR and powder X-ray diffraction (PXRD) for the clathrate hydrate samples formed from IPA with CH_4 as a coguest. The experimental results obtained provide useful information on the structure transition and guest−host behaviors in the clathrate hydrates.

EXPERIMENTAL METHODS

The experimental apparatus for the clathrate hydrate phase equilibria was specifically designed to measure the clathrate hydrate dissociation pressures and temperatures accurately. The cell content was vigorously agitated using an impeller-type stirrer. When the pressure depression due to the clathrate hydrate formation reached a steady-state condition, the temperature increased in 0.1 K increments with sufficient time, and accordingly, the cell pressure increased with the clathrate hydrate dissociation. After all clathrate hydrates were dissociated with the increasing temperature, the cell pressure slightly increased again due to the thermal expansion. The H−L_W−V equilibrium points at each pressure and temperature condition were determined using the intersection between the clathrate hydrate dissociation and thermal expansion lines.

The structure of the IPA semiclathrate and CH_4 + IPA gas hydrates was determined by a Rigaku Geigerflex diffractometer (D/Max-RB) by using graphite-monochromatized Cu $K\alpha 1$ radiation ($\lambda = 1.5406$ Å). The XRD data were collected by step mode with a fixed time of 3 s and a step size of 0.02° for $2\theta = 10°−60°$ at 123.15 K. The obtained patterns were analyzed by the Checkcell program.

A Bruker 400 MHz solid-state NMR spectrometer was used in order to identify clathrate hydrate structure and guest distributions. The NMR spectra were recorded at 243 K and

atmospheric pressure by placing the clathrate hydrate samples within a 4 mm o.d. Zr rotor that was loaded into the variable-temperature (VT) probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with magic-angle spinning (MAS) between 2 and 4 kHz. A pulse length of 2 μs and pulse repetition delay of 10 s under proton decoupling were employed when a radio frequency field strength of 50 kHz corresponding to 5 μs 90° pulses was used. The downfield carbon resonance peak of adamantane, which was assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. A more detailed description of the experimental methods has been provided in previous papers.[17−20]

RESULTS AND DISCUSSION

The IPA semiclathrate hydrate [$(CH_3)_2CHNH_2 \cdot 8H_2O$] is not a true clathrate hydrate because the primary amine group is hydrogen-bonded to the water framework structure.[16] The structure of IPA·8.0H_2O semiclathrate hydrate contains octahedral ($4^6 6^2$), dodecahedral (5^{12}), tetradecahedral ($4^2 5^8 6^4$), and hexadecahedral ($5^{12} 6^4$) cages. The amine molecules are hydrogen-bonded within the tetradeca- and hexadecahedral cages.[16] Figure 1 shows the PXRD patterns for
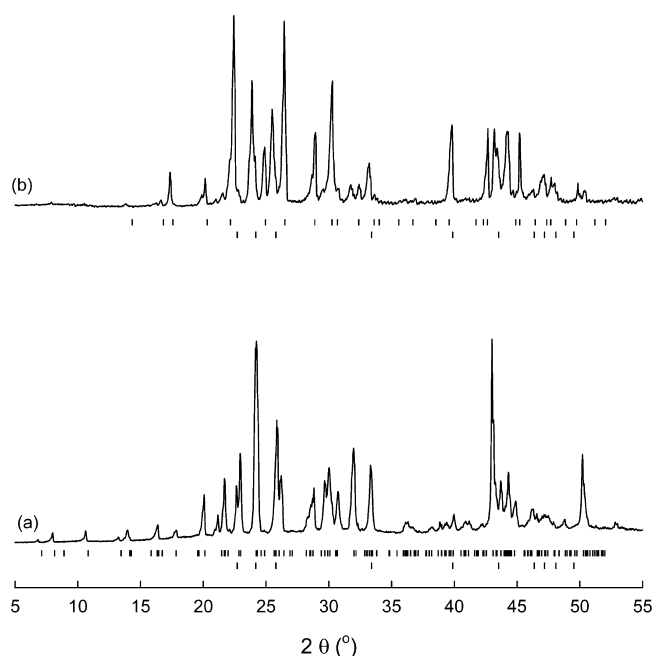

Figure 1. Powder X-ray diffraction patterns at 123.15 K: (a) pure IPA semiclathrate hydrate, hexagonal $P6_3/mmc$, $a = 12.52$ Å, $c = 24.83$ Å, where upper and lower tick marks correspond to hexagonal IPA semiclathrate and hexagonal ice, respectively, and (b) CH_4 + IPA gas hydrate, cubic (sII) $Fd3m$, $a = 17.47$ Å, where upper and lower tick marks represent cubic sII hydrate and hexagonal ice, respectively.

both the pure IPA semiclathrate hydrate and the double CH_4 + IPA gas hydrate at 123.15 K. The structure of pure IPA semiclathrate hydrate was reported to be hexagonal (space group $P6_3/mmc$) with a unit cell dimension of $a = 12.30$ Å and $c = 24.85$ Å.[16] The calculated lattice parameters of the hexagonal ($P6_3/mmc$) IPA·8.0H_2O semiclathrate hydrate formed in this study were 12.52 and 24.83 Å, in good agreement with those obtained from the single crystal structure previously reported in the literature.[16] From Figure 1, the

double CH_4 + IPA gas hydrate was found to be a cubic ($Fd3m$) sII hydrate with a unit cell parameter of 17.47 Å. This clearly indicates that the CH_4 pressurization caused a structural transformation of the pure IPA semiclathrate hydrate to a sII hydrate and the CH_4 molecules acted as coguests in the sII hydrate.

The three-phase (H−L_W−V) equilibria for the CH_4 + IPA + water mixtures were experimentally measured at three different IPA concentrations of 1.0, 5.6, and 11.1 mol % in order to determine the stability conditions of the double CH_4 + IPA gas hydrates. The overall experimental results are summarized in Table 1 and presented in Figure 2. The pure CH_4 forms sI

Table 1. Clathrate Hydrate Phase Equilibrium Data for the CH_4 + IPA + Water Systems

1.0 mol %		5.6 mol %		11.1 mol %	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
275.0	1.99	278.8	2.02	277.3	2.02
279.2	3.63	283.5	3.65	281.6	3.48
282.4	5.28	286.2	5.28	285.1	5.33
285.1	7.30	288.9	7.26	287.8	7.58
288.3	9.64	290.6	9.66	289.8	9.64

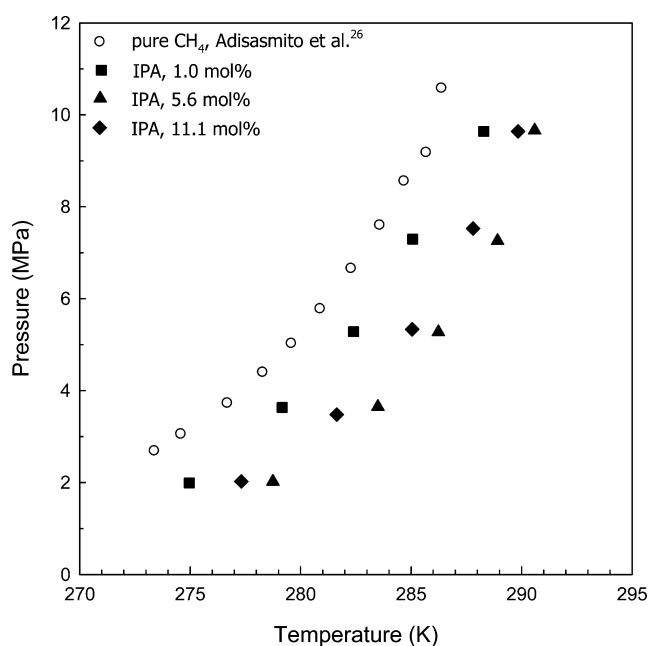**Figure 2.** Clathrate hydrate phase equilibria for the CH_4 + IPA + water mixtures.

hydrates and the IPA molecules form IPA·8.0H_2O semi-clathrate hydrates under atmospheric pressure conditions.[1,16] As can be seen from Figure 2, the H−L_W−V equilibrium conditions of the double CH_4 + IPA gas hydrates were significantly shifted to the stabilized regions that are represented by higher temperature and lower pressure conditions when compared with the pure CH_4 gas hydrate system. The double CH_4 + IPA gas hydrate systems were more stabilized when the IPA concentration increased from 1.0 to 5.6 mol %. However, a lower stabilization effect was observed at 11.1 mol % IPA. As revealed in the PXRD measurements, the double CH_4 + IPA gas hydrates have a sII structure, and thus, 5.6 mol % IPA corresponds to the stoichiometric concentration of a sII hydrate when the IPA molecules are assumed to only

occupy the large $5^{12}6^4$ cages of the sII. Therefore, the maximum stabilization effect was observed at 5.6 mol % IPA. The stabilizing effects of the IPA observed in the clathrate hydrate phase equilibria were caused by the structural transformation of the pure sI CH_4 gas hydrate into the double sII CH_4 + IPA gas hydrates due to the inclusion of the IPA molecules in the clathrate hydrate lattices.

In this study, ^{13}C MAS NMR measurements were undertaken in order to analyze the solid phase of the pure IPA semiclathrate hydrate and the double CH_4 + IPA gas hydrates. NMR spectroscopy was chosen because it has been recognized as a powerful tool for the structure identification and quantitative determination of the hydrate composition and cage occupancy.[21] In particular, the cage-dependent ^{13}C NMR chemical shifts for the enclathrated guest molecules can be used to determine the structure types of the formed clathrate hydrates. Figure 3a shows a stacked plot of the ^{13}C MAS NMR spectra of the pure IPA semiclathrate and double CH_4 + IPA gas hydrates with three different concentrations of IPA (1.0, 5.6, and 11.1 mol %). The pure IPA (11.1 mol %) semiclathrate hydrate exhibited four resonance peaks at 42.7, 42.4, 25.7, and 24.9 ppm. The IPA $[(C_\beta H_3)_2 C_\alpha HNH_2]$ molecules occupy both tetradecahedral ($4^2 5^8 6^4$) and hexadecahedral ($5^{12}6^4$) cages of the semiclathrate structure.[16] In the IPA semiclathrate hydrate, the resonance peaks at 42.4 and 24.9 ppm can be assigned to the α-carbon ($-CH_2-$) and β-carbon $[(CH_3)_2-]$ captured in the tetradecahedral ($4^2 5^8 6^4$) cages, respectively, and the resonance peaks at 42.7 and 25.7 ppm to the α-carbon ($-CH_2-$) and β-carbon $[(CH_3)_2-]$ captured in the hexadecahedral ($5^{12}6^4$) cages, respectively. When CH_4 was introduced into the pure IPA semiclathrate hydrate, the crystal structure was transformed to a sII hydrate, which was also confirmed by the PXRD patterns. In the CH_4 + IPA (11.1 mol %) gas hydrate, there were peaks detected at 42.6, 26.5, and −4.7 ppm in addition to those from the pure IPA semiclathrate hydrate. The chemical shift at −4.7 ppm can be assigned to the CH_4 molecules enclathrated in the small 5^{12} cages of the sII hydrate, while the chemical shifts at 42.6 and 26.5 ppm to the α-carbon ($-CH_2-$) and β-carbon $[(CH_3)_2-]$ captured in the hexadecahedral ($5^{12}6^4$) cages of the sII hydrate, respectively. It should be noted that even though the hexadecahedral ($5^{12}6^4$) cages are common in both semiclathrates and gas hydrates, there is a chemical shift difference between the IPA molecules captured in each hexadecahedral ($5^{12}6^4$) cage. This can be attributed to the difference in the configuration of the IPA molecules in each hexadecahedral ($5^{12}6^4$) cage. In the IPA semiclathrate hydrate, the IPA molecules are hydrogen-bonded within the hexadecahedral ($5^{12}6^4$) cages while in the CH_4 + IPA gas hydrate, the IPA molecules are nonbonded in the hexadecahedral ($5^{12}6^4$) cages.[16] In particular, the chemical shift of β-carbon $[(CH_3)_2-]$ at 25.7 ppm for the semiclathrate hydrate was found to move to 26.5 ppm for the double sII gas hydrate, which indicates that the atomic environment of the IPA β-carbon has been deshielded due to the introduction of the CH_4 gas and the subsequent structural transformation of the semiclathrate hydrate into the sII hydrate. The chemical shift of the α-carbon ($-CH_2-$) captured in the hexadecahedral ($5^{12}6^4$) cages of the sII hydrate was detected at 42.6 ppm. There must be also signals at 42.4 and 42.7 ppm from the α-carbon captured in the tetradecahedral ($4^2 5^8 6^4$) and hexadecahedral ($5^{12}6^4$) cages of the pure IPA semiclathrate, which was formed from the excess IPA molecules. However, the IPA α-carbon captured in the hexadecahedral ($5^{12}6^4$) cages
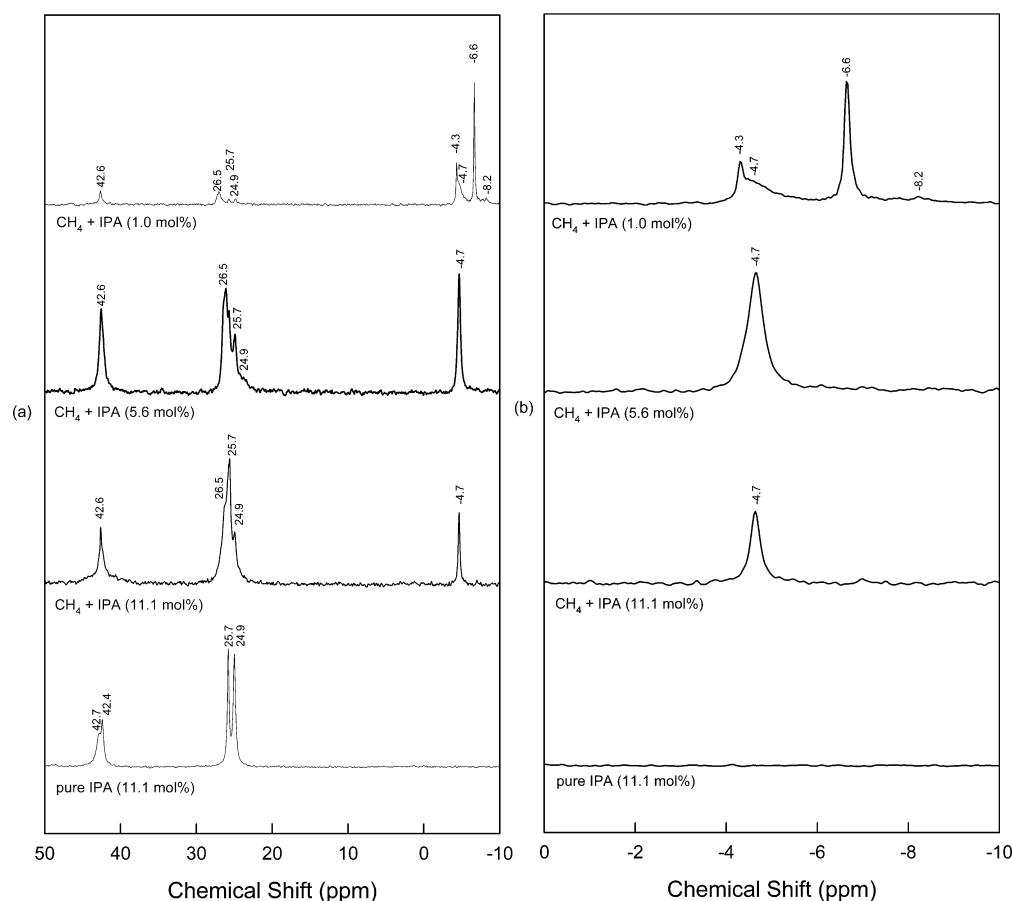
Figure 3. ^{13}C MAS NMR spectra of the pure IPA semiclathrate and CH_4 + IPA gas hydrates (a) in a full scale and (b) in an expanded scale.

Table 2. ^{13}C NMR Chemical Shifts of the Guest Molecules in the IPA Semiclathrate and CH_4 + IPA Gas Hydrates

	IPA semiclathrate		CH_4 + IPA gas hydrate (sII)	
	tetradecahedra ($4^2 5^8 6^4$)	hexadecahedra ($5^{12} 6^4$)	dodecahedra (5^{12})	hexadecahedra ($5^{12} 6^4$)
α-carbon ($-CH_2-$)	42.4	42.7	–	42.6[a]
β-carbon [$(CH_3)_2-$]	24.9	25.7	–	26.5
CH_4	–	–	−4.7	−8.2

[a]Not distinguishable from α-carbon captured in the tetradecahedral ($4^2 5^8 6^4$) and hexadecahedral ($5^{12} 6^4$) cages of the semiclathrate due to the very close appearance and merging of each resonance peak.

of the sII hydrate was not distinguishable from that captured in the tetradecahedral ($4^2 5^8 6^4$) and hexadecahedral ($5^{12} 6^4$) cages of the semiclathrate due to the very close appearance and merging of each resonance peak. The ^{13}C NMR chemical shifts of the guest molecules in the IPA semiclathrate and CH_4 + IPA gas hydrates are listed in Table 2.

In the CH_4 + IPA (5.6 mol %) gas hydrate, signals from the pure IPA semiclathrate were remained, but their intensity was significantly lowered. The chemical shift of the CH_4 molecules (at −4.7 ppm) captured only in the hexadecahedral ($5^{12} 6^4$) cages also supports the formation of the sII hydrate. At an IPA concentration of 1.0 mol %, a considerable amount of the pure CH_4 gas hydrate (sI) was observed as well as the CH_4 + IPA gas hydrate (sII). The resonance peaks at −4.3 and −6.6 ppm can be assigned to the CH_4 molecules captured in the small 5^{12} cages and large $5^{12} 6^2$ cages of the sI hydrate, respectively. Furthermore, the additional peak at −8.2 ppm can be assigned to the CH_4 molecules captured in the large $5^{12} 6^4$ cages of the sII hydrate. For water-soluble or insoluble sII hydrate-forming guests, the coexistence of sI and sII hydrates is sometimes

observed at lower concentrations than the stoichiometric concentration of the sII hydrate and is caused by the additional reaction of CH_4 with the unreacted water.[22−25] The area ratio of the large $5^{12} 6^2$ (at −6.6 ppm) to small 5^{12} (at −4.3 ppm) cages occupied by CH_4 molecules was 3.25 (in case of full occupancy of CH_4 molecules in the small 5^{12} cages and large $5^{12} 6^2$ cages of the sI hydrate it was 3.0), which again verifies the formation of the pure CH_4 hydrate. However, for the double CH_4 + IPA gas hydrate, the area ratio of the large $5^{12} 6^4$ (at −8.2 ppm) to small 5^{12} (at −4.7 ppm) cages occupied by the CH_4 molecules was 0.16 (in case of full occupancy of CH_4 molecules in the small 5^{12} cages and large $5^{12} 6^4$ cages of the sII hydrate it was 0.5), which indicates that a small amount of CH_4 molecules can also occupy the sII large $5^{12} 6^4$ cages, that are primarily occupied by the IPA molecules. The structural transformation of the IPA semiclathrate hydrate into a sII hydrate as a result of the inclusion of CH_4 as a coguest can be clearly confirmed by both the chemical shift movement of the IPA β-carbon and the cage-dependent ^{13}C NMR chemical shifts of the CH_4 molecules captured in the clathrate hydrate lattices.

It should be noted that even though IPA semiclathrate hydrate structure also contains empty dodecahedral (5^{12}) and hexadecahedral ($5^{12}6^4$) cages, which are in common with sII hydrates, the crystal structure of the IPA semiclathrate hydrates was found to be transformed into sII in the presence of CH_4 as a coguest. However, such a structural transformation by introducing CH_4 was not observed in the QAS semiclathrate hydrates formed from TBAB or TBAF, which maintain their original structures and accommodate the CH_4 molecules in the initially vacant 5^{12} cages.[19,20] It is expected that the structural transformation examined in this study is caused by modifying the hydrophobic−hydrophilic balance through the addition of hydrophobic gases such as CH_4 to the systems. In TBAB or TBAF semiclathrate hydrates, the tetra-n-butylammonium cations are too large to be incorporated into the cages of the sII hydrate structures, and thus, semiclathrate structures form where the anions are incorporated into the hydrogen-bonding network of the water. The water molecules form cage structures that are sufficiently large to capture the tetra-n-butylammonium cations, and accordingly, the TBAB or TBAF semiclathrate hydrates do not exhibit structure changes with the introduction of CH_4. However, in the CH_4 + IPA gas hydrates in this study, the amine molecules are small enough to occupy the sII large cages, and with the CH_4 gas molecules as a coguest, the alkyl chains make the environment sufficiently hydrophobic that the sII hydrate remains stable.

CONCLUSIONS

The experimental results obtained in this study demonstrated for the first time that a structural transformation of the IPA semiclathrate hydrates could occur when small-sized hydrophobic CH_4 molecules were added as coguests to the systems. The precise nature and unique pattern of this structural transformation were closely investigated through the macroscopic phase behavior and microscopic analyses using PXRD and solid-state NMR. In particular, at a low IPA concentration, due to the relative lack of IPA molecules and excess of water molecules, the structural coexistence of pure CH_4 hydrate (sI) and double CH_4 + IPA hydrate (sII) was observed; furthermore, the possible occupancy of the CH_4 molecules in the large $5^{12}6^4$ cages of the sII was also confirmed. These results indicate that the guest gas distribution and the composition of clathrate hydrates can be altered with adjustment in the IPA concentration in the presence of CH_4 as a coguest. Therefore, IPA can be regarded as a candidate for an effective water-soluble liquid hydrate promoter for application in gas storage and transportation areas after understanding the cage occupancy behavior, structural details, and guest−host interactions in the guest + IPA clathrate hydrates.

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Notes
The authors declare no competing financial interest.

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