Spectroscopic Identification of Amyl Alcohol Hydrates through Free OH Observation

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In this study, we identify the crystal structures of amyl alcohol + CH$_4$ hydrates and demonstrate that the free OH observation of alcohol hydrates provides evidence of OH incorporation into the host framework occurring in some amyl alcohols. While two amyl alcohols, 3-methyl-2-butanol and 2-methyl-2-butanol, were identified as encaged in the $5^{12}6^8$ large cage of structure-H hydrate, as expected from their molecular sizes above 7.5 Å, two other amyl alcohols, 3-methyl-1-butanol and 2,2-dimethyl-1-propanol, were identified to be abnormally included in the $5^{12}6^4$ large cage of structure-II hydrate in spite of their too large sizes of 9.04 and 7.76 Å, respectively. The Raman spectra of two "normal" amyl alcohol hydrates evolved free OH peaks around 3600 cm^{-1}, implying that there is no strong hydrogen bonding interaction between alcohol guest and water host; however, for two "abnormal" amyl alcohol hydrates, the corresponding peaks were not detected, which indicates that the OH is incorporated into the host lattice in order to make the large alcohol guest fit into the relatively small $5^{12}6^4$ cage of structure-II. The present findings are expected to provide useful information for a better understanding of alcohol guest dynamic behavior that might be significantly affected by structural dimensions and host−guest interactions.

Simple alcohols such as methanol and ethanol have been known to be thermodynamic inhibitors for hydrate formation, and thus, a lot of related research with high significance has been reported for a long time, particularly in the gas hydrate community.[1−5] Most of these works have been focused on preventing hydrate formation and promoting hydrate dissociation for flow assurance and natural gas recovery.[4,5] However, the principal role of alcohols in hydrate formation has not been seriously treated in this field with full consideration of structural and hydrogen-bonding effects.

Bobev and Tait reported that methanol showed the kinetic promotion effect on hydrate formation due to its hydrophilic OH group as well as the thermodynamic inhibition effect.[6] In addition, it was reported that some alcohols, such as 1-propanol (1-PrOH), 2-propanol (2-PrOH), and *tert*-butyl alcohol (TBA), acted as a structure-II (sII) former in the presence of CH$_4$ gas.[7−9] The 2-PrOH + CH$_4$ and TBA + CH$_4$ hydrates exhibited better thermodynamic stability than pure CH$_4$ hydrate. Therefore, the alcohols as hydrate formers, which possess both kinetic and thermodynamic promotion functions, might offer a considerable option for gas storage and transportation using gas hydrates. Recent research[10,11] reported an interesting phenomenon for 3-methyl-1-butanol (3-Me-1-BuOH), one of the amyl alcohol isomers. The 3-Me-1-BuOH (Figure 1f, 9.04 Å) is known to form a structure-H (sH) hydrate in the presence of Xe,[10] but Ohmura et al.[11] showed that this alcohol forms sII hydrate with CH$_4$. The gauche form of 3-Me-1-BuOH even appears to be too large to be enclathrated into a large $5^{12}6^4$ cage of sII hydrate (sII-L).[1,12,13]

In this study, we synthesized eight structural isomers of amyl alcohol + CH$_4$ hydrates and analyzed their crystalline structures using solid-state high-power decoupling (HPDEC) ^{13}C NMR spectroscopy and powder X-ray diffraction (PXRD). In particular, Raman spectroscopy was used in order to explain abnormal enclathration of some amyl alcohols through "free OH" observation.

The molecular size of a hydrate former has been recognized as one of the key factors in determining the hydrate structure.[1] In view of guest inclusion, a molecular size above 7.5 Å is considered to be too large to be fitted into sII-L.[1] To check the molecular dimensions of amyl alcohols, the optimum structures were determined by Gaussian 03.[12] The B3LYP method with the 6-311 ++ G (d, p) basis set was used for this calculation. The calculated molecular size of amyl alcohols (7.76−10.33 Å) in Figure 1 implies that sH might be exclusively formed with CH$_4$.[1] First, the amyl alcohol + CH$_4$ + water hydrate samples were identified by HPDEC ^{13}C NMR spectroscopy. As shown in Figure 2a, four amyl alcohol samples—1-pentanol (1-PeOH), 2-pentanol (2-PeOH), 3-pentanol (3-PeOH), and 2-methyl-1-butanol (2-Me-1-BuOH)—show only two peaks representing CH$_4$ signals in the small 5^{12} cage (sI-S, $\delta = -4.5$ ppm) and large $5^{12}6^2$ cage (sI-L, $\delta = -6.9$ ppm) of structure-I (sI) hydrate, confirming that only pure CH$_4$ hydrate formed without any appearance of binary amyl alcohol + CH$_4$ hydrate; thus, we excluded these alcohols from any further consideration. On the contrary, in Figure 2b, two amyl alcohols of 3-methyl-2-butanol (3-Me-2-BuOH) and 2-methyl-2-butanol (2-Me-2-BuOH) show two peaks representing CH$_4$ signals in the small 5^{12} cage (sH-S, $\delta = -4.7$ ppm) and middle $4^35^66^3$ cage (sH-M, $\delta = -5.1$ ppm) of sH hydrate. The area ratio of two peaks ($A_{sH\text{-}S}/A_{sH\text{-}M}$)

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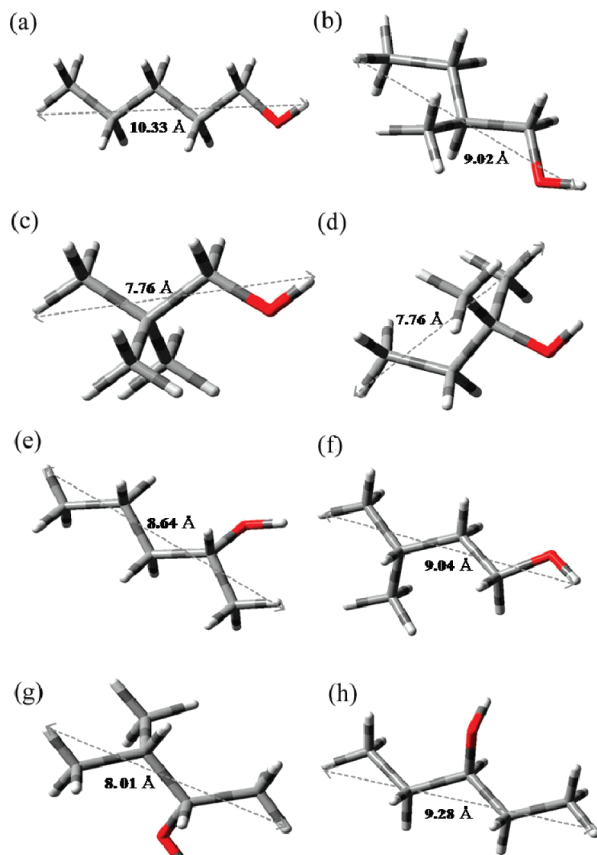
Letters

J. Phys. Chem. B, Vol. 113, No. 31, 2009 **10563**

Figure 1. Structures and end-to-end distances[13] of eight isomers of amyl alcohol calculated by Gaussian 03:[12] (a) 1-pentanol (1-PeOH); (b) 2-methyl-1-butanol (2-Me-1-BuOH); (c) 2,2-dimethyl-1-propanol (22-DiMe-1-PrOH); (d) 2-methyl-2-butanol (2-Me-2-BuOH); (e) 2-pentanol (2-PeOH); (f) 3-methyl-1-butanol (3-Me-1-BuOH); (g) 3-methyl-2-butanol (3-Me-2-BuOH); (h) 3-pentanol (3-PeOH). The molecular sizes of all amyl alcohols are suitable to be enclathrated into the sH-L.

Figure 2. (a) HPDEC ^{13}C MAS NMR spectra of amyl alcohols. (b) Magnified NMR spectra of 3-Me-1-BuOH + CH$_4$, 22-DiMe-1-PrOH + CH$_4$, 3-Me-2-BuOH + CH$_4$, and 2-Me-2-BuOH + CH$_4$ hydrates.

Figure 3. PXRD patterns of (a) 3-Me-1-BuOH + CH$_4$, (b) 22-DiMe-1-PrOH + CH$_4$, (c) 3-Me-2-BuOH + CH$_4$, and (d) 2-Me-2-BuOH + CH$_4$ hydrates. The diffraction peaks of hexagonal ice and sI hydrate as an impurity were marked by asterisks (*).

is checked to be approximately 1.5; this value shows a good agreement with those of common sH hydrates in the literature. Two additional peaks at $\delta = -4.5$ ppm and $\delta = -6.9$ ppm in the spectrum of 3-Me-2-BuOH indicate that pure CH$_4$ hydrate also coexists in this sample. The PXRD patterns of these two amyl alcohol hydrates were determined as shown in Figure 3c and d; their structures were confirmed to be the hexagonal *P6/mmm* ($a = 12.208(21)$ Å, $c = 9.901(49)$ Å for 3-Me-2-BuOH and $a = 12.198(42)$ Å, $c = 10.005(53)$ Å for 2-Me-2-BuOH).[14] The cell parameters are agreeable with the reported values of $a = 12.26$ Å and $c = 10.17$ Å for the sH hydrate.[1] The stable enclathration of these two relatively large amyl alcohol guests into host water framework structures formed hydrates to sH, as demonstrated here by NMR and PXRD. These results are quite natural and well expected wherever large guests are involved.

However, an unnatural inclusion pattern of amyl alcohols was observed from the remaining two amyl alcohol hydrates. In the ^{13}C NMR spectra of 3-methyl-1-butanol (3-Me-1-BuOH) and 2,2-dimethyl-1-propanol (22-DiMe-1-PrOH) samples shown in Figure 2b, two peaks representing CH$_4$ signals in the small 5^{12} cage (sII-S, $\delta = -4.7$ ppm) and large $5^{12}6^4$ cage (sII-L, $\delta = -8.3$ ppm) are detected. These two samples were also checked by PXRD (Figure 3a and b)[14] and identified as the cubic *Fd3m* structures ($a = 17.268(31)$ Å for 3-Me-1-BuOH and $a = 17.346(8)$ Å for 22-DiMe-1-PrOH). For 3-Me-1-BuOH, Ohmura et al.[11] identified in their recent research that this hydrate forms a sII structure. Although isopentane, another sH hydrate former,
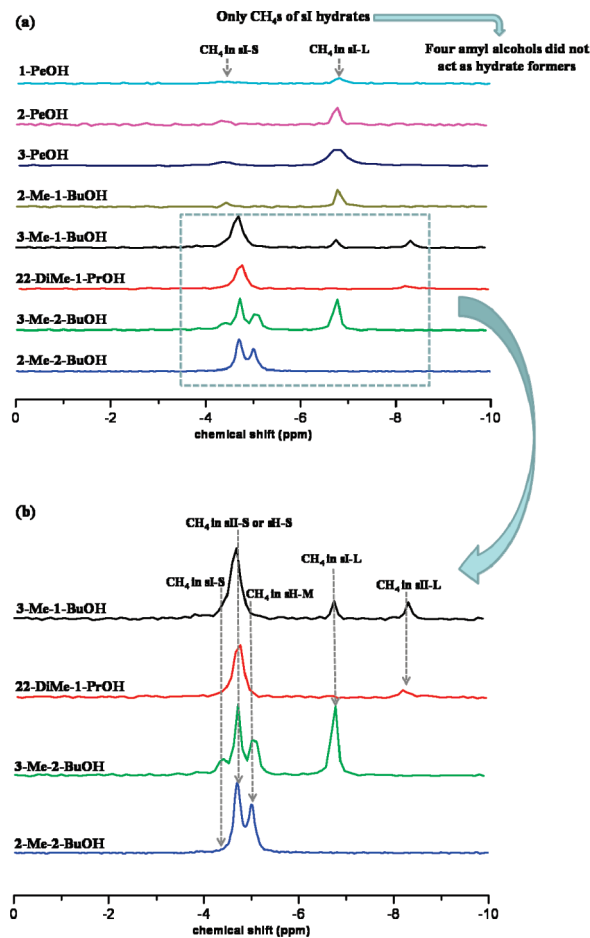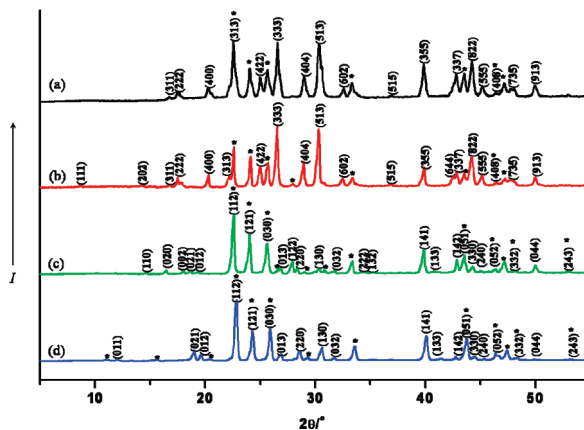
was reported to be enclathrated into sII-L as a gauche conformation, quite a little amount of isopentane can be included only with the coexistence of neopentane, a sII hydrate former.[15] As shown in Figure 2b, only a small fraction of CH$_4$ occupies sII-L at $\delta = -8.3$ ppm, implying that the sII-L is dominantly occupied by 3-Me-1-BuOH and 22-DiMe-1-PrOH for these two hydrate samples. At the present stage, it might be worthwhile to recognize that specific structural types of large alcohol hydrates can form sII.
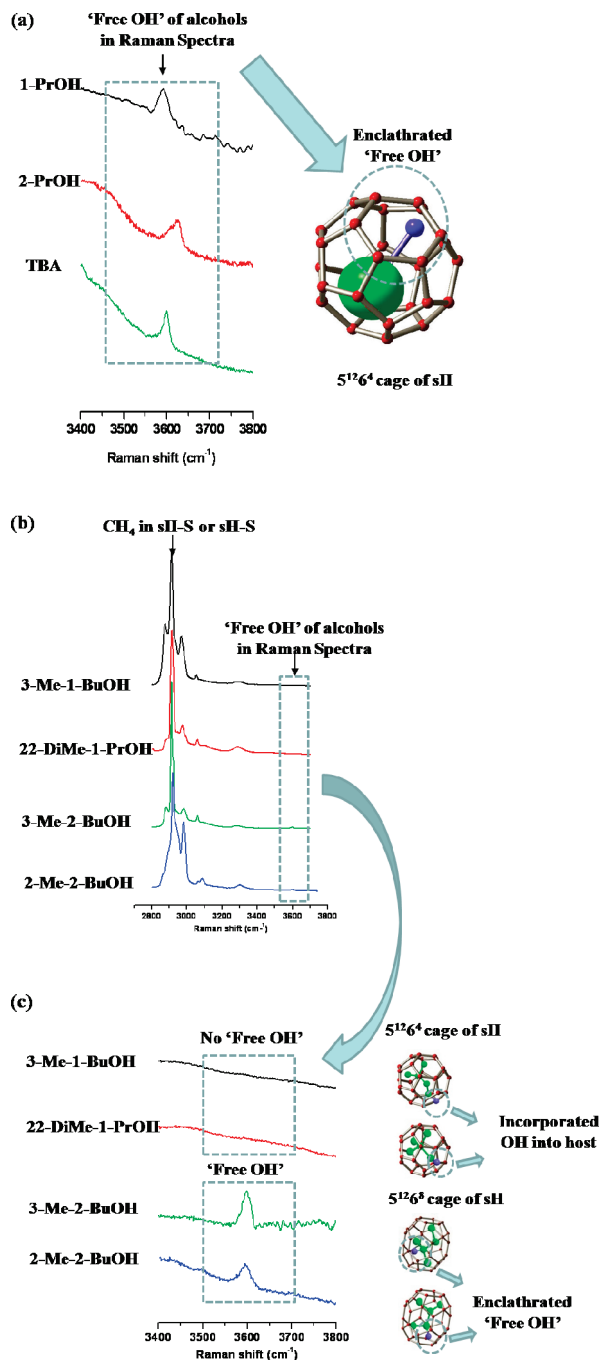
Figure 4. Raman spectra of (a) 1-PrOH + CH$_4$, 2-PrOH + CH$_4$, and TBA + CH$_4$ hydrates in the range of the free OH region, (b) 3-Me-1-BuOH + CH$_4$, 22-DiMe-1-PrOH+ CH$_4$, 3-Me-2-BuOH + CH$_4$, and 2-Me-2-BuOH + CH$_4$ hydrates in the range from 2700 to 3600 cm^{-1}, and (c) Magnification of part b in the range of the free OH region. For the clear observation of free OH peaks, D$_2$O was used. (Red balls, O in water; blue ball, O in alcohol; green ball (large), hydrophobic group in alcohol; green balls (small), C in alcohol; hydrogen atoms in host frameworks are omitted).

Accordingly, a key question arises as to what really influences the lattice dimension and cage framework structuring after large alcohol guest inclusion. In the Raman spectroscopy, the O−H stretching mode commonly appears as a strong and broad peak around 3200 cm^{-1} because of its hydrogen-bonding interaction. In contrast, the non-hydrogen-bonded O−H stretching mode, called the "free OH bond", is observed as a weak and sharp peak around 3600 cm^{-1} in dilute alcohol solutions with nonpolar solvents.[16−18] Alcohol guest included in clathrate hydrate, which
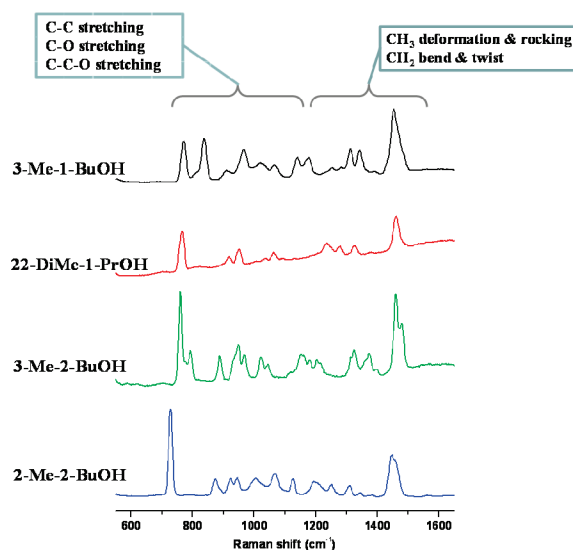

Figure 5. Raman spectra of 3-Me-1-BuOH + CH$_4$, 22-DiMe-1-PrOH + CH$_4$, 3-Me-2-BuOH + CH$_4$, and 2-Me-2-BuOH + CH$_4$ hydrates in the range from 600 to 1600 cm^{-1}.

can also be called the "solid solution", is considered to be a similar instance to the latter. Water must be a highly polar solvent, but water molecules composing cage lattices become four-connected with neighboring ones, thus causing alcohol guests to have relatively weak interaction with host water lattices. In the previous study, we observed the free OH bond of TBA at 3610 cm^{-1} in the Raman spectrum of TBA + CH$_4$ hydrate, which confirms the formation of "genuine" clathrate hydrate without hydrogen bonding between TBA in sII-L and the water host (Figure 4a).[7] Here, we additionally observed the free OH bond around 3600 cm^{-1} for sII alcohol hydrates of 1-PrOH + CH$_4$ and 2-PrOH + CH$_4$, as shown in the spectrum of Figure 4a.[8,9] Thus, we might conclude that the "ordinarily encaged" alcohol guests have no hydrogen bonding interaction with host water and evolve the free OH bond signal around 3600 cm^{-1}. We additionally note that the gauche form of 1-PrOH is expected to have a suitable size to sII-L as *n*-butane does, while its trans form is too long to be enclathrated into sII-L.[1] With this Raman pattern representing the free OH bonds, we further tested four amyl alcohols. Each sample shows the C−H stretching mode due to CH$_4$ in sII-S or sH-S at 2913 or 2914 cm^{-1} (Figure 4b). We focused on the peak existence around 3600 cm^{-1}; the spectra are shown in Figure 4c. Apparently, the 3-Me-2-BuOH and 2-Me-2-BuOH encaged in sH-L show their free OH bonds, but for 3-Me-1-BuOH and 22-DiMe-1-PrOH, the identical peaks around 3600 cm^{-1} were not detected, which indicates that the OH is incorporated into the host lattice in order to make the large alcohol guest fit into the relatively small 5^{12}6^4 cage of structure-II. The role of OH appears to be quite similar to incorporation of anions such as C$_2$H$_5$CO$_2^-$ or CH$_3$SO$_3^-$ occurring in quaternary ammonium salt hydrates.[19,20] Additionally, we present the C−C and C−O stretching modes of 3-Me-1-BuOH + CH$_4$, 22-DiMe-1-PrOH + CH$_4$, 3-Me-2-BuOH + CH$_4$, and 2-Me-2-BuOH + CH$_4$ hydrates in Figure 5.[21]

In this study, we attempted to identify the crystal structures of amyl alcohol + CH$_4$ hydrates and demonstrated that their free OH existence might be a key factor in determining the cage dimensions as well as the hydrate structure type. In view of practical applications, the relatively high solubility of some alcohols in water might provide direct advantages for preparation, storage, and transportation.

Letters

J. Phys. Chem. B, Vol. 113, No. 31, 2009 **10565**

Supporting Information Available: Experimental methods and NMR and Raman spectra details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The end-to-end distances of eight isomers of amyl alcohol were calculated by Gaussian 03, and van der Waals diameter of H atom (2.4 Å) added.

(14) The PXRD patterns were indexed using the Check Cell program. LMGP-Suite Suite of Programs for the interpretation of X-ray Experiments, by Jean laugier and Bernard Bochu, ENSP/Laboratoire des Matériaux et du Génie Physique, BP 46. 38042 Saint Martin d'Hères, France. http://www.inpg.fr/LMGP and http://www.ccp14.ac.uk/tutorial/lmgp/.

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