Phase Behavior and Structural Characterization of Coexisting Pure and Mixed Clathrate Hydrates

Yu-Taek Seo,[b] Huen Lee,[b] Igor Moudrakovski,[a] and John A. Ripmeester*[a]

KEYWORDS:
clathrates · host±guest systems · hydrates · phase transitions · NMR spectroscopy

Clathrate hydrates are crystalline compounds formed by a physically stable interaction between water and relatively small guest molecules.[1] Under suitable conditions of guest pressure and temperature, water molecules, via hydrogen bonds, form into polyhedral cavities that connect to give space-filling frameworks. Because of partial cage filling, these crystalline compounds are nonstoichiometric. They can be divided into three distinct structural families I (sI), II (sII), and H (sH), which differ in their combination of cavities of different sizes and shapes.[2] Although the above hydrate structures with natural gas components as guest molecules are widely known, new structures continue to be reported, such as a new, highly complex structure, known as structure T (sT) hydrate, that contains two cages of unusual geometry,[3] and a new sII ± sH polytype.[4] As well, a metastable sII hydrate of xenon has been observed: when a sII hydrate of tetrahydrofuran (THF) was placed in contact with hyperpolarized xenon.[5] It is clear that many of the physical attributes of clathrate hydrates remain unknown and need to be identified in more detail.

In our previous work, multiphase equilibria were measured to examine the complex phase behavior in the hydrate stability region for aqueous solutions containing carbon dioxide and methane as secondary guests.[6] Although normally a single phase is expected to be stable in such systems, here we report the coexistence of sI and sII phases in a ternary system consisting of methane, THF, and water. This system was chosen especially to examine which structure would appear, depending on the relative concentration of the water-soluble THF molecules. THF by itself forms sII hydrate in a completely miscible aqueous solution,[7] and in this structure, because of their size, THF guests occupy only the large 51264 (H) cages. Furthermore, the mixed hydrate formed by THF and methane guests has been identified as sII, and this is independent of the THF to water ratio.[8] However, stable hydrates in THF ± methane systems may have widely varying overall compositions, as methane may well occupy some of the large, as well as small, cages. In order to determine this, we followed two specific THF concentrations, 5.6 and 3.0 mol%,[2] during hydrate formation. As an indirect measure of hydrate formation, the pressure ± temperature (P ± T) trajectory,[1] which represents hydrate nucleation, growth, and dissociation stages, was measured experimentally and the resulting closed loop made by the hydrate formation and dissociation processes is shown in Figure 1a. The mixed CH4 + THF hydrate started to form directly after going through the three-phase equilibrium boundary,[2] and rapid pressure reduction occurred immediately after hydrate formation.

![Figure 1](image-url)

Figure 1. Hydrates formed from aqueous 5.6 mol% THF solution. a) P ± T trajectory representing one stage of hydrate formation/dissociation. b) 13C NMR spectra of the mixed CH4 + THF hydrate at point A.

[a] Dr. J. A. Ripmeester, Dr. I. Moudrakovski
Steacie Institute of Molecular Sciences
National Research Council of Canada
Ottawa, ON, K1A 0R6 (Canada)
Fax: (+1) 613 998 7833
E-mail: John.Ripmeester@nrc-cnrc.gc.ca

[b] Y.-T. Seo, Prof. H. Lee
Department of Chemical Engineering
Korea Advanced Institute of Science and Technology
373-1, Kusong-dong, Yusong-gu
Daedeon 305-701 (South Korea)
Upon complete transformation of the 5.6 mol% aqueous (THF·17H₂O) THF solution to hydrate. The system pressure continued to decrease almost linearly with temperature, which indicates that further hydrate formation did not occur, even after passing the three-phase equilibrium boundary of pure methane hydrate. As the temperature was again raised to approach the phase boundary of the mixed hydrate, the system pressure abruptly increased because of complete dissociation. For structure identification, the ¹³C NMR spectrum (Figure 2b) of the mixed hydrate sample, obtained at point A (Figure 1a), was measured (using a Bruker 400 MHz solid-state NMR spectrometer). There is a single methane resonance line at -4.50 ppm, which means that methane molecules occupied the smaller sII D cages, but not the larger sII H cages. On the contrary, THF molecules resided in the H cages, as identified by the two resonances at 25.9 ppm (-C–C–) and 68.0 ppm (-C–O–C–). Although the stoichiometric ratio of D to H cages is known to be 2:1 in the unit cell of sII, the relative integral intensities of the ¹³C NMR spectra confirmed the absolute cage occupancies of θ_LCH₄ = 0.3684, θ_SCH₄ = 0, and θ_LTHF = 0.9948 (S = smaller, L = larger). These NMR spectroscopic results show that the THF molecules completely occupied the sII H cages, and the methane molecules partially occupied the sII D cages.

In particular, we found an unusual P–T trajectory when an aqueous 3 mol% THF solution (thus considerably below the ideal stoichiometry of the mixed hydrate of 5.6 mol% [1,2]) was cooled, as shown in Figure 2a. The first pressure reduction, which indicates that again a mixed CH₄ + THF hydrate formed just below the expected phase boundary of the mixed hydrate, is similar to that for the 5.6 mol% THF mixture shown in Figure 1. Subsequently, further cooling initiated a second pressure drop below the phase boundary of pure methane hydrate, suggesting that

Figure 2. Hydrates formed from aqueous 3 mol% THF solution. a) P–T trajectory representing two stages of hydrate formation/dissociation. b) ¹³C NMR spectra of the mixed CH₄ + THF hydrate at point B. c) ¹³C NMR spectra of the coexisting mixed CH₄ + THF and pure CH₄ hydrates at point C.
pure methane hydrate formed as well. Upon warming, a sudden pressure increase, because of hydrate dissociation, was observed near the phase boundaries of both the pure and mixed hydrates. It is quite surprising that the P–T trajectory shown in Figure 2a has two stages of pressure reduction, and it is clear that a new hydrate structure that is different from sII has appeared. To identify the hydrate structures formed before and after the second pressure reduction, 13C NMR spectra were obtained for the mixed hydrate samples at points B and C (Figure 2a), and these are shown in Figures 2b and c, respectively. For the mixed hydrate at point B, located just above the phase boundary of pure methane hydrate, the NMR spectrum confirmed that THF molecules occupied a large fraction of sII H cages, whereas methane molecules occupied only sII D cages, and this situation is nearly identical to that observed for the mixed CH4 + THF (5.6 mol%) hydrate. The resulting absolute cage occupancies were found to be $\theta_{\text{CH}_4} = 0.5924$, $\theta_{\text{CH}_4} = 0$, and $\theta_{\text{THF}} = 0.9906$.

When the temperature was reduced to point C, the unexpected spectral characteristics of methane hydrate appeared as two resonances at $-4.34$ ppm and $-6.67$ ppm: these were identified as methane molecules in the S1(D) and S26(T) cages of sII hydrate,[10] respectively. The ratio of the integral intensities of methane in the sII D to T cages was determined to be $I_D/I_T = 0.3223$, which is almost identical to the ideal stoichiometric ratio (1/3) of D to T cages in the case of sI. Accordingly, it can be concluded from examining the P–T trajectory and NMR data that pure methane hydrate formed and coexisted with mixed CH4 + THF hydrate in the low temperature region, after passing through the phase boundary of pure methane hydrate.

We also note that methane molecules occupied quite a large proportion of the small sII D cages at point C. The NMR spectrum shown in Figure 2c confirmed that the absolute cage occupancies of the two coexisting hydrates were $\theta_{\text{CH}_4} = 0.9272$, $\theta_{\text{CH}_4} = 0$, and $\theta_{\text{THF}} = 0.8041$ for the mixed CH4 + THF hydrate (sII) and $\theta_{\text{CH}_4} = 0.9282$, $\theta_{\text{CH}_4} = 0.9599$ for the pure methane hydrate (sI). On moving from point B to point C, both new sII and more sII hydrate were formed, as confirmed by NMR spectroscopy at point C. Even in this case, the occupancy of CH4 molecules in sII H cages was not observed. However, some additional experiments have shown that upon decreasing the concentration of THF further, the occupancy of the large cages (sII H) by methane becomes quite significant: $\theta_{\text{CH}_4}/\theta_{\text{THF}} = 0.23$ for a THF concentration of 0.1 mol%. The detailed NMR results of cage occupancy, along with the corresponding phase behavior, could not be used to ascertain whether the additional formation of new sII and more sII hydrate at point C was initiated by converting the earlier formed solid mixed CH4 + THF hydrate or unreacted, free, liquid water. To clarify this, we used 1H NMR microimaging. D2O–THF and CD4 were used to eliminate possible contributions to the images from the protons in the methane and THF molecules. Small THF hydrate particles and ice (≈1.0 mm) were formed by freezing and grinding a 3 mol% D2O–THF solution. It was then loaded into a high-pressure tube, which was inserted into the cold (250 K) imaging probe of a 400 MHz NMR spectrometer. After the tube was pressurized with CD4 up to 50 bar, the temperature was increased to 285 K, which was considered to be high enough to initiate the melting of both ice and pure THF hydrate. The resulting images are shown in Figure 3. In Figure 3A, a very intense 1H resonance signal arose, as shown by the bright spots (which represent the liquid aqueous phase) in the image. However, the THF solution formed a mixed hydrate with methane under the specified pressure, temperature, and THF concentration, as can be seen by the evidence of crystallization: aggregates of particles, in images a–f. Although the tube’s contents were continuously converted to the mixed solid CD4 + D2O–THF hydrate, there was always liquid phase present in the bulk, which thus confirms the presence of liquid water available for the methane hydrate formation at point B in the P–T space.

To confirm the formation of a sII hydrate of pure methane with the remaining water, the temperature was reduced to 275 K, slightly higher than the freezing point of ice, but lower than the formation temperature of pure methane hydrate. On a longer timescale, all bright areas were converted almost completely to dark areas, indicating that the free liquid water was used to form pure methane hydrate. The formation processes for pure systems having a single host component appear to be more complicated than expected for mixed systems with multiguest components. We can conclude from this work that the solid hydrate formed initially did not reorganize, even when the equilibrium conditions were changed markedly. After the initial mixed hydrate formation lowered the THF concentration, addi-
tional hydrate formed as the solution was cooled, but the composition reflected the lower concentration of THF. So, first of all, we observed the small cages being filled with methane, as the occupancy of the large cages by THF decreased. Eventually, the methane also replaced some THF in the large cages. When the THF concentration was sufficiently low, pure sI methane hydrate was formed when the appropriate phase boundary was crossed, thus giving a complex mixture of solid phases.

The present study can be considered to be a first attempt to explore the microscopically complex behavior of mixed hydrates in heterogeneous states through hydrate phase equilibrium determination, NMR spectroscopic analysis of cage occupancy, and microimaging observation to follow water consumption.

This research was performed for the Carbon Dioxide Reduction and Sequestration Center, one of the 21st Century Frontier R & D programs funded by the Ministry of Science and Technology of Korea and also partially supported by the Brain Korea 21 Project.

Quasiharmonic Vibrations of Water, Water Dimer, and Liquid Water from Principal Component Analysis of Quantum or QM/MM Trajectories

Ralph A. Wheeler,* Haitao Dong, and Scott E. Boesch[a]

KEYWORDS:
ab initio calculations ∙ density functional calculations ∙ molecular dynamics ∙ water ∙ vibrational spectroscopy

Dramatic experimental advances allow measurements of vibrational frequencies for molecules in condensed phases to determine polymer conformations, protein folds and folding pathways, and enzyme mechanisms,[1, 2] but computational approaches to assist in mode assignments for condensed-phase vibrations have not kept pace. Traditional methods for calculating molecular vibrations are based on solving an eigenvalue problem formulated from Wilson FG matrices.[3] Solvent effects on molecular vibrations may be incorporated by using a continuum solvent model[4] or adapting classical molecular dynamics (MD),[5] quantum MD,[6] or QM/MM[7] programs to construct a Hessian matrix and solve the eigenvalue problem at a series of time steps. These methods are all limited by the harmonic approximation. Continuum solvent models are incapable of replicating specific solute-solvent interactions, and dynamics methods require considerable computer time to construct and diagonalize the Hessian matrix at each time step. Fourier transform-based methods[8, 9] cannot be used with Monte Carlo simulations, give vibrational frequencies but not the associated modes, and/or require longer trajectories to resolve closely spaced vibrational frequencies.[10, 11] This contribution demonstrates the capabilities of multivariate statistical analysis[12, 13] of quantum MD or QM/MM trajectories to calculate vibrational frequencies for an isolated water molecule, water dimer, and liquid water. Tests were chosen to determine the accuracy of principal mode analysis (PMA) for calculating intramolecular vibrations of small molecules, intermolecular vibrations involving noncovalent contacts, and vibrations of small molecules in a condensed phase. Unlike conventional matrix diagonalization methods, PMA incorporates some anharmonicity and performs a time average before solving a single eigenvalue equation. Compared to transform-based methods, PMA requires shorter trajectories, typically gives lower frequencies, and gives vibrational modes in addition to frequencies.

[a] Prof. Dr. R. A. Wheeler, H. Dong, S. E. Boesch
Department of Chemistry and Biochemistry
University of Oklahoma
620 Parrington Oval
Norman, OK 73019 (USA)
Fax: (+1)405-325-6111
E-mail: rawheeler@chemdept.chem.ou.edu

References:

Received: November 5, 2002 [Z571]