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Direct Measure of the Hydration Number of Aqueous Methane

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The aqueous solution properties of methane have long been of interest in many areas. Methane is the simplest hydrocarbon molecule and has often been considered to be a good model compound for understanding the hydrophobic interactions that are important in protein folding and membrane assembly. It is now generally believed that the nature of hydrophobicity is size dependent.[1−3] Small apolar molecules such as methane have a hydration free energy near ambient conditions that is largely entropic; that is, it depends more on the number of ways all of the water molecules in the methane hydration shell can form hydrogen bonds rather than their energies. Hence, the number of water molecules in the solvation shell of small apolar molecules, n_H, is of central importance.

The low aqueous solubility of methane makes experimental studies of this system difficult. Estimates of $n_H = 16$ and 19 have been calculated from the methane carbon−water oxygen radial distribution function determined from neutron diffraction.[4,5] Results from computer simulations indicate that n_H is in the range 16−22.[6−8] A calculation based on the number of water molecules in a spherical shell[9] surrounding methane yields $n_H = 14$, while a methane cavity surface area[10] method gives $n_H = 17$. In this Communication we report the first direct measurement of the hydration number of an aqueous solution of methane that resulted from our ongoing studies of a class of materials called clathrate hydrates.

We are primarily interested in the region of the water−methane phase diagram where methane clathrate hydrates (methane hydrate) form under deep-ocean and permafrost conditions, that is, temperatures near the freezing point of water and pressures greater than 3.5 MPa. Methane forms structure I hydrate, a structure that contains two dodecahedral (20 water molecules) and six tetrakaidecahedral (24 water molecules) water cages per unit cell.[11]

A typical ^{13}C magic-angle spinning (MAS) NMR spectrum of a methane hydrate sample recorded at 243 K and 1.4 MPa is shown in Figures 1a and 1Sa (Supporting Information). Figure 1a shows three resonance lines with chemical shifts of −3.6, −5.9, and −10.3 ppm assigned to methane in the dodecahedral hydrate cage, methane in the tetrakaidecahedral hydrate cage, and methane in the gas phase, respectively.[12−14]

Figures 1b and 1Sb show a ^{13}C MAS NMR spectrum of the partially decomposed methane hydrate obtained at 273 K and 2.6 MPa, and Figures 1c and 1Sc show the ^{13}C MAS NMR spectrum of the completely melted methane hydrate at 275 K and 3.1 MPa. In both parts b and c of Figure 1, the off-scale methane gas-phase peak intensity dominates the ^{13}C MAS NMR spectrum (see Figure 2S, Supporting Information). Note that the methane gas-phase peak chemical shift becomes less shielded as the sample is melted, as expected due to the increased pressure of the sample.[15] For the purposes of the present study, the most interesting feature of the ^{13}C MAS NMR spectra shown in Figures 1 and 1S is the sharp resonance line at −3.7 ppm that appears in the methane hydrate region of the spectrum as the sample is melted. Because only liquid and gas phases are present after the sample is melted, the peak at −3.7 ppm is assigned to aqueous methane.

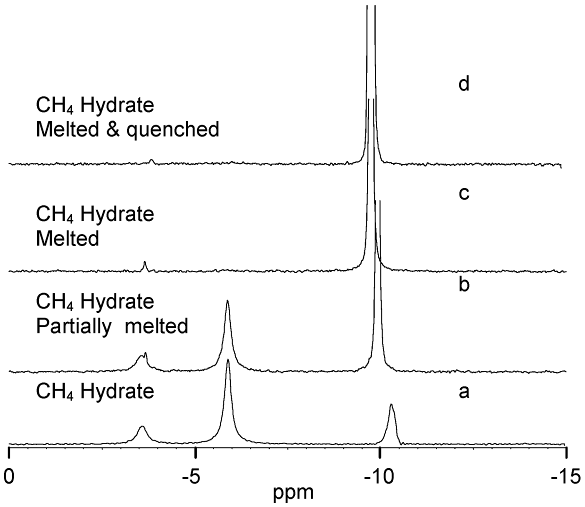

Figure 1. 100.6 MHz ^{13}C MAS NMR spectra of 100% ^{13}C-enriched CH_4 hydrate in various states of decomposition: (a) CH_4 hydrate at 243 K and 1.4 MPa; (b) partially melted CH_4 hydrate at 273 K and 2.6 MPa; (c) completely melted CH_4 hydrate at 275 K and 3.1 MPa; and (d) completely melted and quenched CH_4 hydrate at 253 K and 2.9 MPa.

Further evidence for the assignment of the aqueous methane ^{13}C NMR resonance line is provided by the ^{13}C MAS NMR spectra obtained at 298 K and 1 MPa for a sample of methane + liquid water, Figure 2b,c. Figure 2b shows two resonance lines at −3.7 and −10.5 ppm that each split into the expected quintet, due to *J*-coupling, for the liquid- and gas-phase methane ^{13}C bonded to four equivalent protons when the ^{1}H decoupling is removed, Figure 2c. Thus, the sharp resonance line appearing at −3.7 ppm (Figures 1, 1S, and 2) is clearly due to aqueous methane.

The ^{13}C chemical shifts of methane in methane hydrate and aqueous methane can be used to measure the number of water molecules in the first hydration sphere of methane in both samples because the chemical shift is a measure of cage size or the number of water molecules that are needed to form the cage.[12,13,16] Based on the observation that the ^{13}C chemical shift of aqueous methane is virtually identical to the chemical shift of methane in the dodecahedral cage of methane hydrate, the hydration number of aqueous methane is $n_H = 20$. This n_H value falls within the range observed using other methods.[4−8]

The contrasting behavior of the aqueous methane ^{13}C resonance line and that of methane in the hydrate phase when ^{1}H decoupling is not used is in agreement with the accepted view that no long-lived clathrate cages persist in aqueous solution. Removal of ^{1}H decoupling reveals the *J*-coupling between ^{13}C and ^{1}H in aqueous solution, while in the rigid methane hydrate the ^{13}C resonance lines are severely broadened when ^{1}H decoupling is not used (data not

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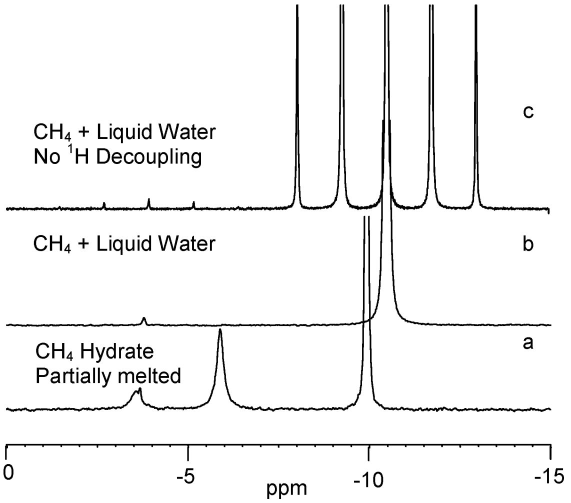

Figure 2. 100.6 MHz ^{13}C MAS NMR spectra of 100% ^{13}C-enriched CH_4 + liquid water and partially melted CH_4 clathrate hydrate: (a) partially melted CH_4 hydrate at 273 K and 2.6 MPa; (b) CH_4 + liquid water sample at 298 K and 1 MPa; and (c) CH_4 + liquid water sample without ^{1}H decoupling at 298 K and 1 MPa.

shown). Hence, the picture of a dynamic aqueous methane hydration shell where water molecules might continuously enter and leave the hydration sphere is consistent with the NMR data presented in this study.

The existence of hydration numbers other than $n_H = 20$ would affect the chemical shift of the aqueous methane ^{13}C resonance line. The small shift toward higher shielding values of the aqueous methane ^{13}C NMR resonance line relative to that of the methane hydrate dodecahedral cage may indicate that some methane molecules have hydration numbers greater than $n_H = 20$. An estimate of the number of aqueous methane molecules hydrated by, say, 21 water molecules can be made on the basis of the linear dependence of the ^{13}C chemical shift of methane on n_H. From the chemical shift and n_H values of methane in the dodecahedral and tetrakaidecahedral cages, a chemical shift value of -4.2 ppm is estimated for a methane molecule with $n_H = 21$. For a simple two-site model the observed chemical shift, δ_{obs}, is given by

$$\delta_{obs} = f_{20}\delta_{20} + f_{21}\delta_{21} = (1 - f_{21})\delta_{20} + f_{21}\delta_{21} \qquad (1)$$

in the limit of fast chemical exchange.[17] f_m is equal to the fraction of methane molecules with $n_H = m$ and chemical shift of δ_m. This simple model yields an f_{21} value of 19%, which should be readily detected in a ^{13}C MAS NMR experiment if this postulated chemical exchange can be stopped. The results of such an experiment are shown in Figures 1d and 1Sd, where the ^{13}C MAS NMR spectrum of the completely melted methane hydrate that was quenched to liquid nitrogen temperature is shown. This type of rapid cooling is expected to freeze-in aqueous methane structures with various hydration numbers. As is clearly shown in Figures 1d and 1Sd, only resonance lines at about -3.8 and about -9.7 ppm are observed; this result is strong evidence that the hydration shell of methane is dominated by values of $n_H = 20$. If a range of hydration numbers is considered, the generalized[17] expression of eq 1 suggests that the populations of these hydration shells may be too small to be detected with the simple freezing-in experiment described here.

On the basis of the ^{13}C MAS NMR results presented in this work, the hydration shell of aqueous methane can be described as one where rather long-lived hydration shells with $n_H = 20$ dominate the methane hydration process but where the methane and water molecule configuration rapidly changes such that rigid methane hydrate dodecahedral cages are not present. The small shift of the aqueous methane resonance line to higher shielding values relative to that of methane in the dodecahedral hydrate cage indicates that the aqueous methane hydration shell is slightly larger than that of the methane hydrate dodecahedral cage.

It is also interesting that the hydration number of aqueous methane corresponds to the magic number of 21 that has been assigned to the dodecahedral cage structure of hydrated H_3O^+, that is, a structure where a central H_3O^+ cation is enclathrated by 20 water molecules.[18] The equality of the hydration number for both methane and H_3O^+ suggests that the similar size of these two solutes determines n_H rather than their apolar or polar nature.

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Supporting Information Available: Sample synthesis, experimental procedures, and ^{13}C MAS NMR spectra of partially melted and melted methane hydrate. This material is available free of charge via the Internet at http://pubs.acs.org.

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