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LETTERS

Hydrate Layers on Ice Particles and Superheated Ice: a ^{1}H NMR Microimaging Study[†]

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Recent observations on the interaction of methane gas with ice surfaces have led to the suggestion that the resulting hydrate layer prevents the encapsulated ice from melting at its usual temperature. This would require ice to exist in a "superheated" state.[1] We have examined the product of the gas−solid reaction with ^{1}H NMR imaging. The imaging experiments show that the hydrate-encapsulated ice is able to melt at its usual melting point. As a possible alternative model, we suggest that a considerable amount of ice inside the hydrate layer can be converted to hydrate and liquid water under isothermal and constant volume conditions, the hydrate layer acting as an insulating, semipermeable layer that insulates processes inside the hydrate layer from external bulk temperature and pressure measurements.

Gas hydrates, or clathrate hydrates, are guest−host compounds in which guest molecules reside in cages formed by hydrogen-bonded water molecules. Guests with van der Waals diameters between ~4.1 and 5.6 Å promote a clathrate known as structure I hydrate[2], a cubic structure with the ideal unit cell $6M_L{\cdot}2M_S{\cdot}46H_2O$ (M_L, M_S are the guest sites associated with the large tetrakaidecahedral and small dodecahedral cages, respectively). Naturally occurring hydrates with methane as guest have been identified both in permafrost and offshore locations.[3,4] Because of their vast extent, these deposits are considered to be a promising source of clean hydrocarbon fuel and also potential agents for climate change. Both for evaluation of the resource potential, as well as assessing the possible impact on climate change, understanding the details of the formation and decomposition of hydrates is of considerable importance. So far, these processes have been studied only by macroscopic techniques, primarily by gas uptake measurements.[5,6] Because of some unusual observations noted during the course of a reaction of methane with ice, it was postulated that superheated ice might exist inside partially reacted ice particles.[1] Hydrate formation from ice involves a number of areas that are of current research interest, including the proper description of the ice surface.[7] In fact, very little is known about hydrate formation at a molecular level.

It has been known for a long time that ice can react with a gas such as methane to yield gas hydrates.[5,8] Gas uptake measurements have shown that initially the reaction proceeds quickly, then slows down markedly unless grinding action provides fresh ice surface for reaction.[5] The observation of an induction time suggests a complex mechanism involving nucleation from precursor states. Recent work[1] in which powdered ice was reacted with methane gas in a closed vessel showed that the gas reacted steadily with the ice when the temperature was increased from ~250 K up to ~293 K and that the pressure and temperature conditions inside the vessel were insensitive to the melting of ice at 273 K. The authors suggested that, in fact, the hydrate layer may have prevented liquid under the hydrate layer from nucleating, and therefore postulated the existence of "superheated" ice.[1] Our experiments

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show that the presence of a hydrate layer on ice does not prevent it from melting, at least not under the conditions of our experiments. We offer a rationale that could explain at least in part the relative isolation of conditions inside partially reacted hydrate particles from the external environment.

Xenon and methane are guest species (G) similar in size, and each forms a structure I hydrate of composition ∼ $G\cdot6.1H_2O$. In the past, we have used ^{129}Xe NMR spectroscopy to obtain significant information on hydrate structure and composition.[9,10] Recently it was shown that NMR spectroscopy with optically polarized xenon increases the sensitivity of the NMR experiment sufficiently to allow the rapid recording of site-specific information on hydrate formation.[11] We have introduced further refinements and improved the sensitivity so that systematic and highly specific information can be obtained on the mechanism of hydrate formation. By measuring the surface area of the ice[12] and the gas uptake, the thickness of the hydrate layer, assuming it to be uniform, is calculated to be in the range of 500 to 1500 Å before the reaction essentially stops on our experimental time scale (∼30 min). The gas−surface reaction can be studied systematically down to 190 K, yielding information on the reaction rate, induction time, and composition.[13] Although it is remarkable that ice reacts rather easily with a hydrate-forming gas even at relatively low temperatures, our main interest is in what happens to the hydrate-coated particle on warming. Does the ice inside the hydrate crust in fact survive warming above 0° C? We have used ^{1}H NMR microimaging techniques to examine hydrate-coated ice particles[14] as a function of temperature from 250 to 276 K. Both xenon and methane have been used as the hydrate-forming gases, with entirely consistent results. The experimental arrangement is shown in the inset of Figure 1. The outer tube, filled either with water or ice particles, serves as an indicator of temperature. Although the temperature control of the probe is better than 0.2 °C, the temperature gradient over the volume of the sample can be as large as 1°.[15] In Figure 1A, the outer tube contains water and the inner tube contains ice particles about 1 mm in cross-section and the hydrate-forming gas is at a pressure of 57 bar, sufficiently high to nucleate hydrate on the surface. Ice and the solid hydrate lattice are invisible in the imaging experiment (dark areas), as the signals for these components decay very rapidly. To eliminate possible contributions from ^{1}H in methane gas in the clathrate, CD_4 was used. Under these conditions the only signal observable must arise from ^{1}H in liquid water (bright areas). At 272.9 K, it can be seen that melting occurs in the outer tube owing to the presence of small temperature gradients in the imaging probe. In all of the experiments A−D (Figure 1), the first signs of melting inside the inner tube also occur at the same temperature. We note that from the NMR images, especially experiments illustrated in Figure 1A and 1D, the integrity of the particles is maintained, as expected for water confined inside a hydrate shell. The intact particle morphology was also confirmed visually. Figure 1B shows a variation on the experiment; the outer tube as well as the inner tube are filled with powdered ice of particle size 0.1−0.2 mm, and the gas pressure for the inside tube was 28 bar. On warming the sample it can be seen that the outside looks essentially the same as the inside: at 273.3 K, both show essentially a water phase. Visually, the tube contents still appeared as a powdered white solid; however, the inside of the particles was completely liquid water. Because of its thinness, the hydrate shell is invisible in the imaging experiment, and only the water inside the particle is visible. For B, in the closed system there is insufficient gas to convert much of the sample so that at 275 K some of the hydrate shells have broken or decomposed and the inner tube shows a continuous region of liquid water with a clump of agglomerated hydrate. At higher pressure, the conversion is greater and more hydrate particles remain intact (Figure 1C). Figure 1D shows the reaction of ice particles with sizes in the range from a fraction of a mm to a few mm with methane at 119 bar. After 10 h at 275 K, the images still show the presence of liquid water confined inside the (invisible to imaging) hydrate shell. These results show conclusively that a hydrate layer does not prevent the encapsulated ice from melting.

We also have carried out some gas uptake experiments in order to estimate the rate and long-term yields of the ice/water−methane reaction.[16] Below 273 K there is a small but rapid uptake of methane gas that corresponds to a conversion of no more than ∼1% of the ice to hydrate. This can be taken as the part of the reaction that corresponds to the hyperpolarized ^{129}Xe uptake experiments described earlier. Gas uptake resumes after the sample temperature reaches ∼273 K. The experiments were continued for ∼40 h and the yield of hydrate was measured as % conversion of ice for samples of different morphologies. At 95 bar of methane and a temperature of 273.5 K, the yields were (sample mass ∼5 g): powdered ice, 74%; ice coarsely crushed at 253 K, 36%; single piece of ice (from melt), 30%. Increasing the reaction temperature to 280.8 K increased the yield to 82% for powdered ice, whereas increasing the pressure to 170 bar increased the yield to 85%. From the rather limited set of experiments, it appears that the long-term yield of the reaction depends mainly on the surface-to-volume ratio of the ice, with smaller effects from temperature and pressure. The initial rate depends mainly on whether the sample was ground or not, suggesting an important role for surface defects.

Although the experiments differ in detail, our results do provide new information that is relevant to the observations in the experiments in which superheated ice was postulated. It is clear that ice inside the hydrate layer is able to melt, at least under the conditions of our experiments. Therefore, the presence of a hydrate layer per se does not prevent liquid water from nucleating.[17] We present some considerations that may help explain why the melting process inside hydrate particles may not be easily observable by monitoring temperature and pressure inside a reaction vessel containing the hydrate. First of all, we consider the volume changes associated with hydrate formation and ice melting. Hydrate formation from ice results in a volume increase of 16.7%. The Pilling−Bedworth rule suggests that the surface reaction should result in a dense surface layer that ultimately limits the reaction.[18] This is indeed observed, and both the Xe uptake and the imaging experiments have shown that the growth of the hydrate layer is quite limited under the conditions of our experiments. Assuming the shell to be mechanically rigid, one may argue that on the time scale of the Xe experiments (∼0.5 h) the hydrate conversion from ice stops because of the increase in volume required inside the shell as ice is converted to hydrate. However as soon as melting starts inside the shell, the volume reduction (ice to water ∼7.8%) would cause some hydrate inside the shell to decompose until the pressure inside the void between water and hydrate is filled with gas at the decomposition pressure of the hydrate. If the hydrate shell acts as a semipermeable barrier, the pressure inside and outside the shell will equalize, thus creating favorable conditions for renewed hydrate formation at the new water−gas−hydrate interface. It is worthwhile to note that the conversion of a fraction of the ice (either directly or via liquid water) to hydrate, which is an exothermic process, can be balanced thermally by the conversion of a portion of the ice to water. In

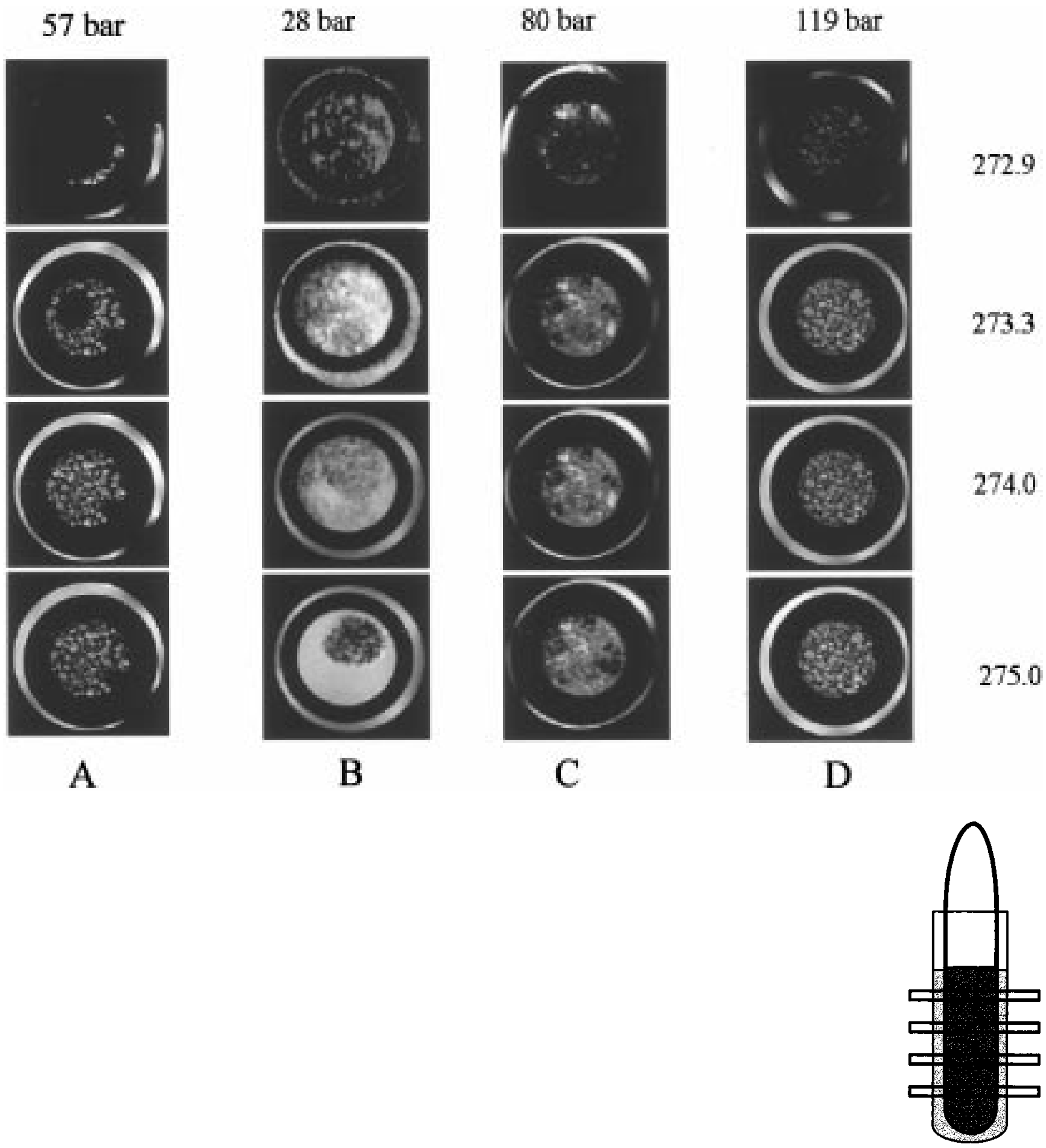

Figure 1. Magnetic resonance images of hydrate-coated ice particles close to the melting point of ice and at different methane-d_4 gas pressures.[20] All images were obtained on a Bruker DSX 400 (magnetic field 9.4T, ^{1}H frequency 400.13 MHz) equipped with a standard Micro2.5 microimaging probe. Multislice spin−echo sequences[21] with a slice-selective 90° pulse of 1 ms were used, with an echo time of 7 ms and a repetition time of 1 s. The images are of 128^2 pixels with a slice thickness of 500 μm in a field of view of 10 mm. The in-plane resolution was about 80 μm using a frequency encode gradient of ∼15 G. Cross-sections at right angles to the long axis of the tube are shown (see inset) with only one slice out of four recorded being shown for each data set (second from bottom, see inset). The outer ring is the reference material (ice/water), the dark ring is the glass tube and the inner circle represents the partially reacted ice−water−hydrate system. Water is visible in these experiments as the bright areas; solid ice and hydrate (as well as the glass tube) are dark. Inset: detail of sample tube showing cross-sections used in the imaging experiments.

this way, about 66% of the ice can be converted to hydrate provided the other 33% of the ice melts. The hydrate layer itself may also play an insulating role, as it is known that clathrate hydrates are very good thermal insulators[19] (a factor of ∼4 better than ice).

Renewed hydrate formation inside the hydrate shell also requires an increase in volume, although the conversion of ice to hydrate, with an increase in volume of ∼16.7% can be balanced in part by the melting of ice with a decrease in volume of ∼7.8%. However, if all of the ice or water inside the shell is to convert to hydrate, eventually the hydrate shell must expand, either gradually through plastic flow or suddenly by rupture. The latter would start a new cycle of relatively rapid hydrate growth. Examination of hydrate formed from small chunks of ice and gas heated above 273 K sometimes shows an “onion skin” structure, confirming a progressive stepwise growth from the outside in. The hydrate coat seems to behave as a semipermeable insulating layer, so that each hydrate-coated ice particle becomes a minireactor in which ice is converted to hydrate in an environment that is only in poor thermal and pressure contact with the volume outside the particles.

In summary, in agreement with previous results, ice reacts with suitable hydrate formers to give hydrate layers at temperatures well below the melting point. When the hydrate-coated ice particle is warmed to temperatures above 0 °C, the ice inside the particle core melts. At sufficiently high gas pressure, water inside the hydrate shell continues to be converted to hydrate. From the relative volume changes and the enthalpies accompanying the various processes, a good fraction of the ice inside the hydrate shell can be converted to hydrate (and water) under isothermal conditions. The insulating character of the hydrate shell may also help to give the reactions inside the shell adiabatic character.

It is clear that the processes involved in forming hydrate from ice are not well understood, and that a considerable amount of work needs to be done in order to test the various models that can be formulated.

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(12) The surface area of the ice was measured by standard BET techniques with N_2 at 77 K. To test the effect of annealing, the samples prepared by crushing ice in liquid nitrogen were kept for an hour at temperatures between 190 and 233 K. The surface area of fresh ice is always in the range of 12−15 m^2/g, which is in good agreement with previously reported data (Adamson, A. W.; Dormant, L. *J. Am. Chem. Soc*. **1966**, *88*, 2055). Annealing leads to about a 3-fold reduction of the surface area as compared to fresh ice. We observed no significant differences in the surface area of the samples annealed at different temperatures, which were between 4 and 5 m^2/g.

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(14) Before measurement, each sample was kept at 273 K for 15−18 h and for 1.5 h at each temperature of measurement.

(15) The temperature gradient in the probe was estimated from multislice images of the melting process of ice in a bundle of 16 glass capillaries.

(16) Gas uptake experiments were carried out in a cylindrical high-pressure cell in which the gas pressure could be controlled by adjusting a precision gas injector. Circulating fluid from a programmable temperature bath controlled the temperature. The cell was loaded with ice (∼5 g) inside a freezer at ∼250 K, evacuated to remove air, pressurized with methane gas, and connected to the circulating bath. The gas injector was adjusted to keep the pressure inside the cell constant as methane was consumed in the conversion to hydrate, and gas uptake was measured from the position of the gas injector piston.

(17) The hydrate and ice Ih structures are incommensurate, and hence there should be an interface that is disorganized, if not liquid, at temperatures near the melting point of ice. We note also the evidence for melting at grain boundaries below the bulk melting point in polycrystalline ice: Salvetti, G.; Tombari, E.; Johari, G. P. *J. Chem. Phys*. **1995**, *102*, 4987. Internal melting at imperfections in single crystals of ice: Gagnon, R. E.; Tulk, C.; Kiefte, H. *J. Glaciology* **1994**, *40*, 132.

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