Experimental Clathrate Dissociations for the Hydrogen + Water and Hydrogen + Tetrabutylammonium Bromide + Water Systems

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Hydrogen has only been recently recognized as a hydrate former, forming structure II hydrate (sII). In this communication, we report new experimental hydrate stability data for the binary hydrogen + water system at pressures ranging from (111.4 to 178.4) MPa and temperature down to 264.45 K. In addition, the formation and dissociation of so-called semiclathrates of hydrogen in the presence of tetrabutylammonium bromide (TBAB) were evaluated. The clathrate and semiclathrate dissociation measurements were conducted using a standard constant volume (isochoric) technique together with step-heating for achieving equilibrium conditions.

Introduction

Hydrogen is currently considered by many as the "fuel of the future". It is particularly favored as a replacement for fossil fuels due to its clean-burning properties; the waste product of combustion being water. Many processes can be used to produce hydrogen (e.g., steam reforming of natural gas, catalytic decomposition of natural gas, partial oxidation of heavy oil, coal gasification, steam-iron coal gasification, water electrolysis, thermochemical, photochemical, photoelectrochemical, and photobiological processes). While hydrogen is relatively easy to produce, there is currently a lack of practical storage methods for molecular H_2, and this is greatly hindering the use of hydrogen as a fuel.

Recent studies have sparked interest in gas (or clathrate) hydrates as potential hydrogen storage materials.[1,2] When trapped into the cages of clathrate hydrates, the distance between gas molecules can approach that of the liquid state, resulting in very high compression ratios. For example, 1 m^3 of structure I (sI) methane hydrate can hold up to 172 m^3 of gas at standard conditions. This has led to considerable research into gas hydrates as a potential means for the storage and transportation of gases. The molecular storage of hydrogen in clathrate hydrates could offer significant benefits with regard to ease of formation/regeneration and cost and safety, as compared to other current storage materials currently under investigation.

Until recently (and for the largely forgotten study of Villard, 1887[3]), hydrogen was considered not to form gas hydrates due to its molecular diameter being too small to stabilize cavities. However, Dyadin et al. (1999)[4] and later on Mao et al. (2002)[1] demonstrated that pure hydrogen can form structure II (sII) clathrate hydrates at very high pressures and low temperatures filling both small and large cavities, which sparked interest in hydrates as a potential hydrogen storage material. In their studies, Mao et al. estimated a storage capacity of 5 wt % given double and quadruple occupancy of H_2 molecules in the small and large cages, respectively. For common sI and sII hydrates, either high pressures (10's of MPa) or low temperatures (subzero) are needed for stability, which introduces significant technical and operational costs. There have been various attempts to increase hydrate stability to lower pressures by employing hydrate "promoters" (e.g., THF, propane). Florusse et al. (2004)[5] showed that the pressure required to stabilize hydrogen in clathrates can be greatly reduced by adding a second guest "promoter", namely, tetrahydrofuran (THF) (≈5 MPa at 279.15 °C). However, these promoters occupy most of the large cavities, reducing the storage capacity.

Lee et al.[6] proposed a method for increasing H_2 content in the THF + H_2 + H_2O system by tuning THF concentration. They claimed double hydrogen occupancy of small cages and multiple hydrogen occupancy of large cages which would result in a higher storage capacity of 4 wt %. However, these results were not reproduced by other researchers who showed a maximum uptake of 1 wt % in the same system.[7−10] A detailed discussion on this controversy can be found elsewhere.[11] Recently, Sugahara et al.[12] observed the presence of H_2 clusters in the large cages of sII by a new method of hydrate preparation. They found that the H_2 storage capacity can increase to 3.4 wt % and depends on the concentration of THF below the eutectic composition of the THF + water binary system, similar to the result of Lee et al.[6]

Even though the DOE 2015 hydrogen storage target of 9 wt % has not been met so far, the research on hydrogen clathrates is still ongoing with the focus on different aspects including the search for new structures[13] and new hydrate forming compounds.[14−16]

Recently, there have been various studies on semiclathrate hydrates of hydrogen.[1,17−19] Semiclathrates are a class of less known hydrates which share many of the same physical and structural properties as common clathrate hydrates, except for the fact that the guest in semiclathrate hydrates may form both parts of the water lattice and occupy cages whereas in normal clathrates the guest molecules are not physically bonded with the water structure.[20] Semiclathrates show much greater stability than normal hydrates. For example, semiclathrates of methane with TBAB dissociate at 293.15 K at 6.5 MPa; however, this is reduced to 282.15 K at the same pressure in the case of normal methane hydrates. Obviously, the difference is higher in the case of hydrogen hydrates. Tohidi et al. patented the use of

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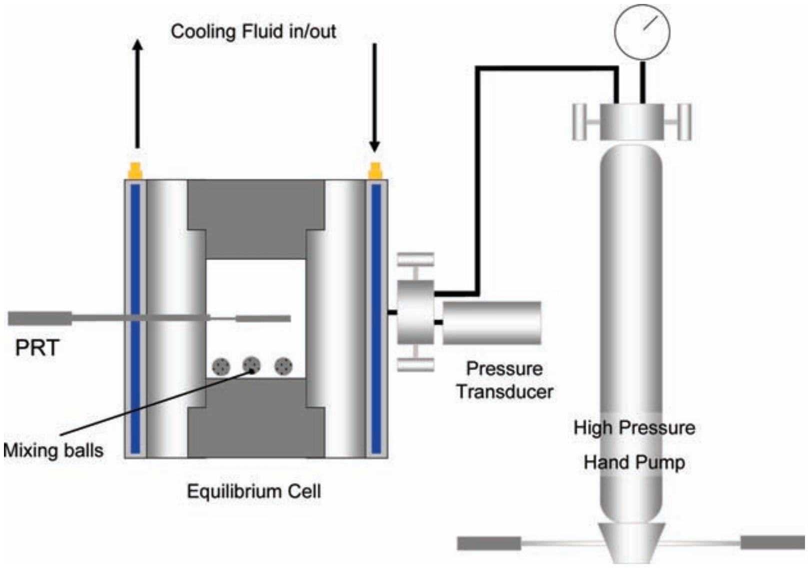

Figure 1. Schematic of the ultrahigh-pressure rig.

semiclathrates as a method for gas storage, transport, and other energy applications.[21]

Tetrabutylammonium bromide (TBAB) is a nonvolatile and nontoxic material that is known to form a number of semiclathrate hydrates with different structures at atmospheric pressures over a range of aqueous salt concentrations.[18,22] These structures have been investigated extensively by Dyadin[22] and Jeffrey and McMullan.[23,24] Five different structures with hydration numbers 24, 26, 32, 36, and 38 are likely to form in the water−TBAB system. However, two main structures, which have been confirmed by other researchers,[25] are those with hydration numbers 26 and 38, referred to as Type A and Type B, respectively. Below 18 wt % TBAB in aqueous solution, Type B is more stable, while at higher concentrations, Type A shows greater stability.[25]

Although the binary phase equilibrium of many semiclathrates has been studied systematically at atmospheric conditions,[22,23] limited work has been carried out with gases under pressure.

Here, we present new experimental hydrate stability data for the sII forming hydrogen + water (up to pressures of 180 MPa) system as well as for the hydrogen + water + TBAB system with a TBAB stoichiometric mass fraction of 0.41.

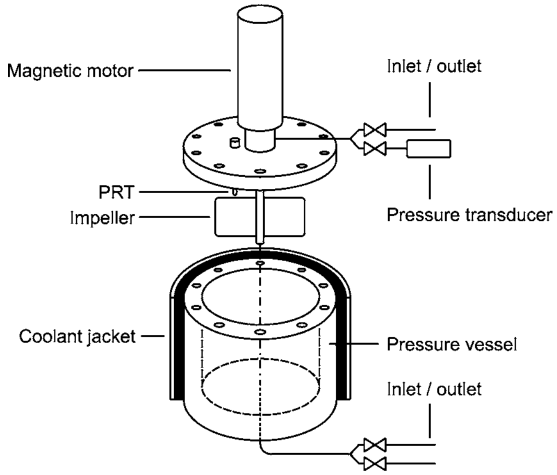

Figure 2. Schematic illustration of the high-pressure rig.

Experimental Section

Clathrate dissociation and/or ice melting *p*,*T* conditions were determined by standard constant-volume isochoric equilibrium step-heating techniques. This method, which is based on the direct detection (from pressure) of bulk density changes occurring during phase transitions, produces very reliable and repeatable phase equilibrium measurements.[26]

Materials. Hydrogen was purchased from BOC gases with a certified volume fraction purity greater than 99.995 %. Tetrabutylammonium bromide solution, $w = 0.50$ in water, was purchased from Aldrich (CAS Number: 1643192). Deionized water was used to dilute tetrabutylammonium bromide to the desired mass fraction in the experiments.

Ultrahigh-Pressure Apparatus. The hydrate setup was used for tests up to 180 MPa. It is comprised of a 45 cm^3 cell constructed of AISI 660 steel. A schematic of the setup is shown in Figure 1. The cell has a maximum working pressure of 200 MPa and can be used with salts and organic liquids. Cell temperature was monitored with a SITEC platinum resistance thermometer (PRT) with the sensing part directly in contact with test fluids. The temperature probe was calibrated against a Prema 3040 precision thermometer. The uncertainty in the temperature measurements was estimated to be better than ± 0.1 K. Cell pressure was measured using a Quartzdyne pressure transducer which has an uncertainty of 0.005 MPa. The calibration of the pressure transducer was checked regularly using a dead weight tester. System temperature was controlled by circulating coolant from a cryostat (JULABO F70) through a jacket surrounding the cell. Mixing was achieved by rocking the cell through 180° using a compressed air-driven mechanism. To aid mixing, stainless steel ball-bearings were placed inside the cell.

High-Pressure Apparatus. Figure 2 shows the apparatus used to determine the phase equilibrium conditions. Phase equilibrium was achieved in a cylindrical cell made of Inconel. The cell volume is about 300 cm^3, and it can be operated up to 40 MPa between (263 and 323) K. The equilibrium cell was immersed in a constant-temperature liquid bath (Lauda Ecoline-Staredition E200). The cryostat is capable of maintaining the cell temperature to within 0.02 K. A platinum resistance probe monitored the temperature and was connected directly to a computer for direct acquisition. The pressure was measured by means of a Druck pressure transducer (Druck PDCR960-50 MPa pressure transducers) mounted directly on the cell and connected to the same data acquisition unit. This system allowed real time

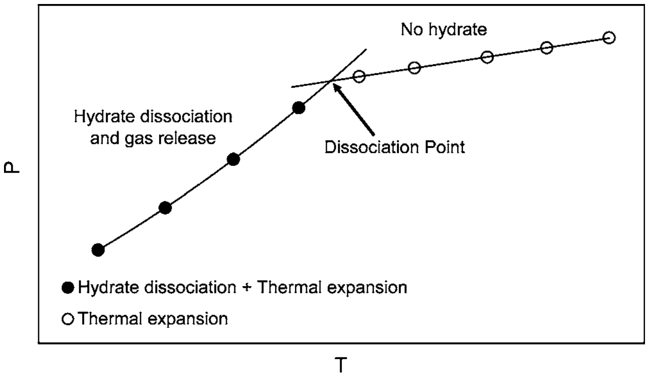

Figure 3. Dissociation point determination from equilibrium step-heating data. The equilibrium dissociation point is determined as being the intersection between the hydrate dissociation (gas release related pressure rise with increasing temperature) and the linear thermal expansion (no hydrate) curves.

readings and storage of temperature and pressure data throughout the different isochoric runs. To achieve a fast thermodynamic equilibrium and to provide a good mixing of the fluids, a high-pressure magnetic stirrer (Top Industrie S.A − wetted parts made of titanium) was used to agitate the test fluids at around 1000 rpm with a rushton-type impeller. The pressure transducer can measure pressure with an uncertainty of 0.008 MPa over the cell operating range.

Experimental Procedures. A typical test to determine the hydrate dissociation point of a system was as follows.

The equilibrium cell was first cleaned and vacuumed, then charged with the desired components. Half of the volume of the cell was initially preloaded with water, then hydrogen was injected to achieve a pressure of 70 MPa. To attain higher pressures, water was subsequently injected using a high-pressure hand pump. The cell temperature was set to a point well outside the expected hydrate stability zone for the system under study during loading. Temperature was then lowered to form hydrates, growth being detected by an associated drop in cell pressure (as gas becomes trapped in hydrate structures). Cell temperature was then raised stepwise (usually 0.5 K intervals), allowing enough time at each temperature step for equilibrium to be reached (sometimes in excess of 24 h). At temperatures below the point of complete dissociation, gas is released from decomposing hydrates, giving a marked rise in the cell pressure with each temperature step (Figure 3). However, once the cell temperature has passed the final hydrate dissociation point and all clathrates have disappeared from the system, a further rise in the temperature will result only in a relatively small pressure rise due to thermal expansion. This process results in two traces with very different slopes on a pressure versus temperature (p,T) plot: one before and one after the dissociation point. The point where these two traces intersect (i.e., an abrupt change in the slope of the p,T plot) is taken as the dissociation point (see Figure 3).

Following measurement of a single dissociation point, cell pressure was increased by injection of water to reach the next desired condition, before the cycle was repeated to determine a further point on the phase boundary for the system.

Table 1. Experimental Clathrate Hydrate Dissociation (H + L + V > L + V) for the Binary System $H_2 + H_2O$ Measured in the Ultrahigh-Pressure Apparatus

T/K (± 0.1)	p/MPa (± 0.005)
269.15	178.41
268.15	160.76
267.15	146.80
266.45	134.97
265.25	120.75
264.45	111.38
Q1[a]: 263.85	105.00

[a] Estimated.

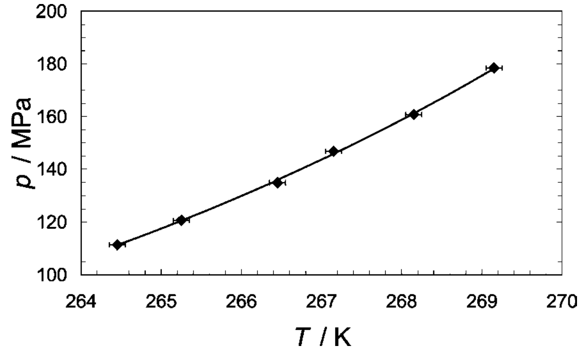

Figure 4. Experimental clathrate hydrate dissociation for the binary system $H_2 + H_2O$ (◆). (Error bars: ± 0.1 K.) (p/MPa) = $3.508 \cdot 10^{-10} \cdot \exp(1.0014 \cdot 10^{-1} \cdot (T/\mathrm{K}))$.

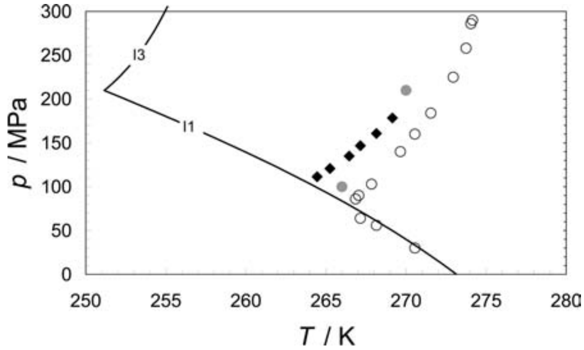

Figure 5. Experimental clathrate hydrate dissociation for the binary system $H_2 + H_2O$ (◆, this work; ○, H_2, data from Dyadin et al.;[4] ●, $D_2 + D_2O$, data from Lokshin and Zhao[27]). I1 and I3 stand for Ice I and Ice III.

Results and Discussion

Measured equilibrium hydrate dissociation conditions are reported in Table 1 and plotted in Figure 4. For the binary system $H_2 + H_2O$, there are some discrepancies in the currently measured data and data previously reported by different authors, deviations sometimes being in excess of 3 K (Figure 5). Dyadin et al.[4] stated that in some experiments equilibrium conditions were not actually achieved, whereas Lokshin and Zhao[27] studied the $D_2 + D_2O$ system. In Figure 6, a typical dissociation point measurement is shown: during cooling, ice is first formed (pressure rise), and then during heating, ice melts and water is converted into hydrate. By further heating, hydrates are dissociated which is characterized by essentially congruent decomposition on the phase boundary.

The quadruple point, Q1—where ice, vapor, liquid, and hydrate coexist for this system (I + V + L + H)—has been estimated. The point where the best fitted curve to our experimental data and the ice I curve intersect is taken as the quadruple point (Figure 6).

The cage occupancy for this system has also been the subject of some debate. Mao et al.[1] were the first to report that hydrogen could form simple cubic structure II clathrate hydrates at high pressures (200 MPa at 280 K) and/or cryogenic temperatures (145 K). Authors estimated a clathrate stoichiometry of $H_2 \cdot 2H_2O$ based on double H_2 occupancy of all 16 small pentagonal dodecahedral (5^{12}) cavities and quadruple occupancy

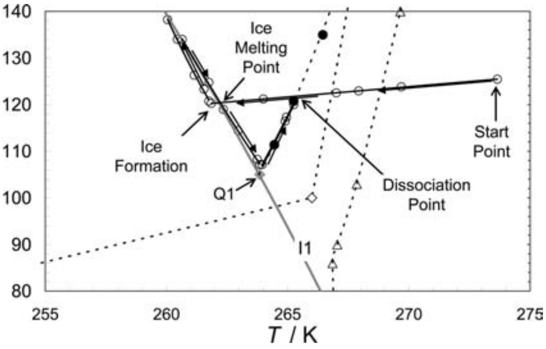

Figure 6. Typical clathrate hydrate dissociation point measurement for the binary system H_2 + H_2O (○, equilibrium points; ◆, estimated Q_1). Experimental clathrate hydrate dissociation points: ●, this work; △, H_2, data from Dyadin et al.;[4] ◇, D_2 + D_2O, data from Lokshin and Zhao.[27]

Table 2. Experimental Hydrate Dissociation for the Ternary System H_2 + TBAB + H_2O with $x_{TBAB} = 0.037$ Measured in the High-Pressure Apparatus

T/K (± 0.1)	p/MPa (± 0.008)
285.95	3.64
286.35	6.43
286.75	10.78
287.15	16.31

of larger hexakaidecahedral ($5^{12}6^4$) cavities, giving a maximum hydrogen storage capacity of 5 mass %. Subsequently, in 2004, Lokshin et al.[2] demonstrated that the large hexakaidecahedral cage can hold up to four hydrogen molecules (two to four depending on T and p), but the small pentagonal dodecahedral cage can hold only one hydrogen molecule, leading to a maximum hydrogen mass fraction of 3.77 %.

The measured dissociation conditions for H_2 + TBAB + water at TBAB mole fraction of 3.7 % which is known to form the most stable semiclathrates[25,28] are shown in Table 2 and plotted in Figure 7. As it has been reported by different authors,[17,19] semiclathrates of hydrogen are formed at significantly lower pressures or higher temperatures than pure hydrogen clathrates. This can be seen from Figure 8 where dissociation data for semiclathrates of TBAB at two different mole fractions ($x = 0.037$ and $x = 0.0062$) have been plotted along with those of hydrogen clathrates.

In the case of TBAB semiclathrates, hydrogen can only be encaged in the small dodecahedral cavities as the larger cages are filled with tetrabutylammonium cations.[18] As a result, the hydrogen storage capacity is largely reduced. Assuming full occupancy of the small cages by hydrogen, the theoretical mass fraction storage capacity is only 0.6 %.

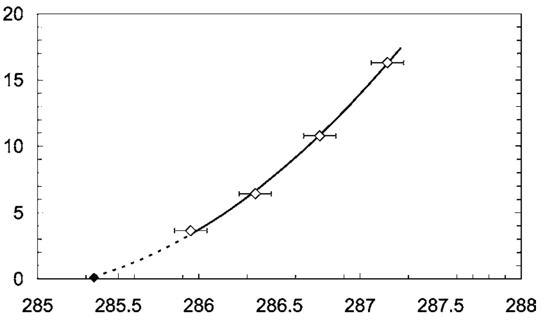

Figure 7. Experimental semiclathrate hydrate dissociation for the ternary system H_2 + TBAB + H_2O (◇, H_2 + TBAB, this work; ◆, TBAB, data from Dyadin et al.[22]). (Error bars: ± 0.1 K.) $(p/\ \mathrm{MPa}) = 2.89261 \cdot (T/\mathrm{K})^2 - 1647.25 \cdot (T/\mathrm{K}) + 234513.29$.

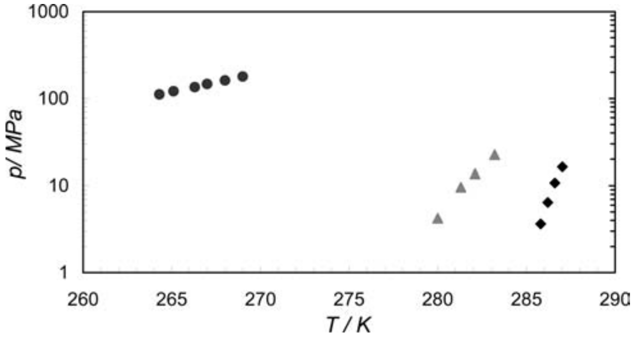

Figure 8. Experimental clathrate hydrate dissociation for the binary H_2 + H_2O and ternary H_2 + TBAB + H_2O systems (●, H_2, this work; ◆, H_2 + TBAB, $x_{TBAB} = 0.037$, this work; ▲, H_2 + TBAB, $x_{TBAB} = 0.0062$, data from Arjmandi et al.[20]).

Conclusions

New experimental hydrate stability data for the sII forming hydrogen + water system and semiclathrate forming hydrogen + water + tetrabutylammonium bromide systems have been generated up to (180 and 16) MPa, respectively. These data provide better delineation of hydrogen stability fields, for which there is a considerable scatter in the data notably for the H_2 + H_2O system.

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