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Low-Pressure Molecular Hydrogen Storage in Semi-clathrate Hydrates of Quaternary Ammonium Compounds

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Clathrate hydrates, or *gas hydrates*, are a group of ice-like, crystalline inclusion compounds which form through the combination of water and suitably sized "guest" molecules, typically under low temperature and elevated pressure conditions. Within the clathrate lattice, water molecules form a network of hydrogen-bonded cavity structures that enclose the guests, the latter generally comprising single or mixed low-molecular-diameter gases and/or organic compounds (e.g., methane, THF).[1]

Previously, the molecular diameter of hydrogen was considered too small to stabilize clathrate cavities, even in hydrates formed from gas mixtures.[1,2] However, recent studies demonstrate that significant H_2 can be accommodated in simple (single guest) and binary cubic structure II clathrate hydrates under specific conditions.[3,4] This discovery has prompted considerable research into clathrate hydrates as potential hydrogen storage materials.[3−7]

In this communication, we report that substantial volumes of molecular hydrogen can be stored in the structural cavities of a class of lesser known clathrate hydrates, namely the semi-clathrate hydrates of quaternary ammonium salts (QAS).[8,9] Phase equilibrium studies of tetra-*n*-butylammonium bromide (TBAB, $(C_4H_9)_4N^+Br^-$) and tetra-*n*-butylammonium fluoride (TBAF, $(C_4H_9)_4N^+F^-$) aqueous systems under H_2 pressure confirm the formation of binary H_2-TBAB and H_2-TBAF semi-clathrate hydrates which are stable at ambient temperatures (≤29 °C) to atmospheric pressure. Such favorable stability conditions, combined with ease of formation/H_2 regeneration and low parent QAS solution vapor pressures (thus high H_2 purity), make semi-clathrates particularly attractive as potential H_2 storage media.

Mao et al.[3] 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 of larger hexakaidecahedral ($5^{12}6^4$) cavities, giving a maximum hydrogen storage capacity of 5 mass %. However, the excessively high pressures required for stability render pure hydrogen hydrate impractical for everyday use as an H_2 storage medium.

In 2004, Florusse et al.[4] reported that hydrogen could be stabilized in clathrates at lower pressures and temperatures close to ambient (∼15 MPa at 10 °C) by means of occupation of the normally vacant dodecahedral cavities of cubic structure II THF hydrates. However, the use of volatile organic compounds such as THF to stabilize H_2 in clathrates introduces a number of problems, most notably contamination of the hydrogen released upon hydrate dissociation. This means that any practical application of the technology would require some secondary separation process to produce a clean fuel. One potential solution to both the pressure and hydrogen purity problems is the storage of molecular H_2 in semi-clathrate hydrates of quaternary ammonium compounds.[8,9]

Semi-clathrate hydrates share many of the physical and structural properties of true clathrate hydrates (structures I, II, and H).[1,10−14] Both hydrate classes comprise a hydrogen-bonded water latticework based primarily around the pentagonal dodecahedra (5^{12}) unit of structure. Structural variety arises from the way dodecahedra associate: face sharing or bonding between vertices adjusting to create a variety of interstitial multifaceted polyhedra for accommodation of (guest) gas molecules or ion pairs without significantly disrupting the hydrogen-bonding scheme of the water framework. The principal difference between the two groups is that, in true clathrate hydrates, guest molecules are not physically bonded to the water lattice; rather, they are held within—and lend stability to—cavities through van der Waals interactions. In contrast, in semi-clathrates, guest molecules both physically bond with the water structure and occupy cavities; for the quaternary (or peralkyl) ammonium salt semi-clathrates, the QAS hydrophobic cation takes a cage filling role, while the negatively charged anion is hydrogen bonded with water latticework.[10−14] Although semi-clathrates are primarily composed of water (often >95 mol % H_2O), this configuration lends great thermal stability to structure, giving some semi-clathrates melting temperatures in excess of 30 °C at atmospheric pressure.[10−14]

A number of authors working on binary QAS−water systems have reported gas bubbles visibly emanating from semi-clathrates dissociating at atmospheric pressure.[10,14] This phenomenon has been attributed to trapping of air molecules in normally vacant cavities, although little work has been done to assess hydrate gas uptake, particularly at elevated pressures where significant enclathration might be expected to occur. Recently, Kamata et al.[15,16] confirmed that H_2S can be incorporated into TBAB semi-clathrate hydrates, most likely by means of occupation of vacant dodecahedral cavities. This leads to the question of whether other gases, in particular hydrogen, can be stored in semi-clathrates.

In this work, semi-clathrate hydrate phase equilibria were determined experimentally for H_2-TBAB$-H_2O$ and H_2-TBAF$-H_2O$ systems for the temperature range 280−310 K up to 25 MPa. For reference, dissociation conditions for binary TBAB$-H_2O$ and TBAF$-H_2O$ clathrates were also measured. In both cases, aqueous TBAB and TBAF solutions were prepared according to the stoichiometry of binary QAS$-H_2O$ clathrates, showing maximum thermal stability at atmospheric pressure. Hydrate stability regions were determined by reliable constant-volume, isochoric equilibrium step-heating techniques.[17]

As shown in Figure 1, H_2-TBAB semi-clathrate formation is clearly observed on cooling from a significant reduction in system pressure and associated exothermal peak. Hydrate formation always occurred at a few degrees of subcooling from the phase boundary, as is typical for kinetically controlled, heterogeneous stochastic nucleation.[1] Step-heating curves were initially linear and approximately equal in slope to liquid + gas (L+G) pressure−

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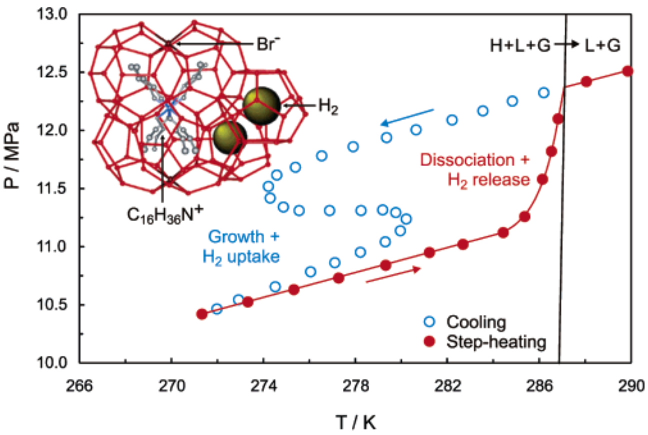

Figure 1. Example of cooling/heating curves for aqueous QAS systems under hydrogen pressure, in this case for H_2−TBAB−H_2O. Inset: Structure around the tetra-*n*-butylammonium cation for TBAB•38H2O, modified after Shimada et al.[18] The dodecahedral cages are available for accommodation of H_2 molecules.

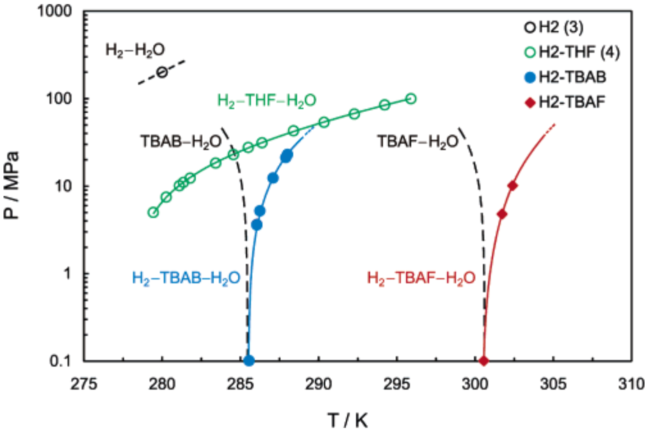

Figure 2. Experimental clathrate dissociation conditions with interpolated phase boundaries for simple (single guest) hydrogen and binary H_2−THF clathrate hydrates (literature data) compared to those for H_2−TBAB and H_2−TBAF semi-clathrate hydrates (this work, ±0.25 K/0.07 MPa).

temperature (*PT*) relations, suggesting complete conversion of the liquid phase to solid clathrate. This is consistent with the use of stoichiometric QAS−H_2O aqueous solutions. Dissociation close to the clathrate phase boundary suggests melting is near congruent.[7]

Measured dissociation conditions and interpolated phase boundaries for H_2−TBAF and H_2−TBAB semi-clathrates are compared with those for simple H_2 and binary H_2−THF clathrate hydrates in Figure 2. TBAB−H_2O and TBAF−H_2O phase boundaries are also shown for reference. Hydrogen uptake into semi-clathrates is confirmed by the obvious shift in clathrate stability regions (from binary phase equilibria) when H_2 is present. Simple TBAB and TBAF semi-clathrates have a slightly lower density than their parent solutions, resulting in melting point depression at elevated pressures (analogous to the ice(h)−water system). The change from a negative to a positive slope of phase boundaries signifies an increase in system bulk density, which is consistent with H_2 molecules being trapped in clathrate cavities. Florusse et al.[4] observed similar behavior for THF clathrate hydrates under H_2 pressure, confirming from NMR spectra that the observed shift in dissociation conditions was the result of binary H_2−THF clathrate formation: hydrogen entering and stabilizing normally vacant dodecahedral THF hydrate cavities. In binary systems, for the aqueous concentrations studied here, TBAB and TBAF both form semi-clathrate hydrate structures where dodecahedral cavities are vacant.[12,18] Given that these cavities are known to accommodate hydrogen in simple and binary H_2−THF clathrate hydrates[3−7] and have been found to host small molecules (H_2S) in TBAB semi-clathrate hydrates, we suggest that they are the primary sites of hydrogen enclathration in the binary H_2−TBAB and H_2−TBAF semi-clathrates discovered here.

Figure 2 shows that binary H_2−QAS semi-clathrate hydrates demonstrate greatly increased thermal and low-pressure stability when compared with H_2 and H_2−THF clathrate hydrates. Simple H_2 hydrates require pressures in excess of 200 MPa at ambient temperatures for stability, and, while the formation of binary H_2−THF hydrates reduces the pressure required for hydrogen enclathration significantly, 100 MPa is still required for stability at room temperature (293 K). Binary H_2−QAS semi-clathrates are considerably more stable: melting temperatures for H_2−TBAF hydrates are ∼302 K (29 °C) at atmospheric pressure.

In addition to more favorable stability conditions, H_2−QAS clathrates have the added advantage that the hydrogen released upon dissociation is extremely pure; chromatographic analysis reveals only trace levels of water. While semi-clathrate H_2 content as a function of pressure, temperature, and QAS:H_2O stoichiometric ratio requires further investigation, standard volumetric analyses of H_2−TBAB hydrates at 1 MPa/283 K yielded 50 vol/vol hydrogen (STP), a value considerably higher than that for H_2−THF clathrates (∼6 vol/vol) at the same pressure.[7] There are a large number of quaternary ammonium (and phosphonium, sulfonium) compounds known to form semi-clathrates of varying structure in binary systems with water; thus, there is significant potential opportunity for optimizing H_2−QAS stability conditions and the volume of hydrogen stored.

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