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Hydrogen Storage in Semiclathrate Hydrates of Tetrabutyl Ammonium Chloride and Tetrabutyl Phosphonium Bromide

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Original calorimetric and phase equilibrium properties for hydrogen + tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBACl), or tetrabutylphosphonium bromide (TBPB) semiclathrate hydrates were measured using differential scanning calorimetry under pressure. The dissociation temperatures of H_2 + TBACl and H_2 + TBPB semiclathrate hydrates are very close to the ambient temperature at low pressures around 15.0 MPa. H_2 + TBACl and H_2 + TBPB systems therefore exhibit better and comparable stability than the H_2 + TBAB system at equivalent pressure, respectively. The amount of hydrogen stored in H_2 + TBACl and H_2 + TBPB semiclathrate hydrates was estimated in terms of the H_2-to-water mole ratio (n_{H_2}/n_{H_2O}) calculated from disssociation enthalpies and (p, T) equilibrium data. In terms of mass fraction deduced from the ratio (n_{H_2}/n_{H_2O}), H_2 + TBACl and H_2 + TBPB semiclathrate hydrates can store 0.12 % and 0.14 % of hydrogen, respectively. Moreover, the quantity of hydrogen stored in these two semiclathrate hydrates is significantly higher than that stored in the H_2 + TBAB system.

Introduction

Gas clathrate hydrates are crystalline compounds formed by physical combination of water molecules linked by hydrogen bonds which constitute cages around guest gas molecules.[1] The research on these compounds were intensified since the 1930s when the petroleum industry first started to search for methods to prevent the formation of natural gas clathrate hydrates in pipelines. Currently they are of interest in different processes such as hydrogen storage and transport of gases[2,3] and for application in natural gas industries.[4] They can exhibit different structures called SI, SII, SIII, SH, SIV, and SVII,[1,3] and typically a high pressure is required to form them.[5]

It was shown for the first time by Fowler et al. in 1940[6] and later by McMullan and Jeffrey[7] that the presence of an additive such as tetraalkylammonium or tetraalkylphosphonium salts considerably reduces the equilibrium pressure of the gas hydrates. Indeed, by using these additives an unusual structure of hydrates called as semiclathrate hydrate is formed, and this one does not require the presence of guest gas molecules to form a stable hydrate structure. Semiclathrate hydrates contain empty cages capable of entrapping some guest gas molecules but differ from the usual gas clathrate hydrates because they include compounds which are not only inserted as guest gas molecules but also form a part of the clathrate cage structure with the hydrogen bonds network built by the water molecules. The particular species capable of promoting semiclathrate structures typically contain a hydrophobic cation made of alkyl groups branched to an ammonium or a phosphonium and a hydrophilic anion. The cation is encaged into the large cavities of the aqueous network, while the anion substitutes to a water molecule in the network.[8–10] This is in contrast to the usual structures of gas clathrate hydrates[1,3] where the host lattice is comprised solely from water. However, gas + semiclathrate hydrates share many of the physical and structural properties of clathrate hydrate structures.

In 2002, some studies demonstrated that significant amounts of hydrogen can be stored in a binary cubic SII clathrate hydrate structure under specific conditions.[11] These studies prompted research into clathrate hydrates as hydrogen storage material.[11–13] However, pure hydrogen clathrate hydrates are impractical for everyday use as a hydrogen storage medium because high pressure is required to form and stabilize them.[5] It was demonstrated in 2004[14] that H_2S can be incorporated into tetrabutylammonium bromide semiclathrate hydrate (TBAB), and later in 2007, volumetric analyses showed that semiclathrate hydrates of TBAB and tetrabutylammonium fluoride (TBAF) can store hydrogen (≈ 0.50 volume fraction at 1 MPa and 283 K for H_2 + TBAB semiclathrate hydrate).[15] TBAB semiclathrate hydrates can store some other gases such as carbon dioxide (CO_2),[16] nitrogen (N_2),[16] methane (CH_4),[16] and some gas mixtures such as (NO_2 + CO_2)[17] and (CH_4 + CO_2).[17] Tetrabutylphosphonium bromide (TBPB) has also demonstrated the capability of entrapping carbon dioxide (CO_2).[18] Moreover, the conditions of formation and stability of the semiclathrate hydrate which are very close to the ambient temperature and the atmospheric pressure make them suitable to a potential hydrogen storage medium. In 2008 Chapoy et al.[19] and Strobel et al.[20] demonstrated that hydrogen can be stored as a binary SH structure, but the minimum pressure required to form the hydrate is 100 MPa. More recently in 2009 it was shown by Prasad et al.[21] that hydrogen storage was possible in the SVI structure double clathrates with tertbutylamine under a pressure of 13.8 MPa but at low temperature (250 K), below the thermal ambient conditions.

In this paper, we report that a more important amount of molecular hydrogen can be stored in semiclathrate hydrates of tetrabutylammonium chloride (TBACl) and TBPB. Molecular hydrogen uptake stored in the compounds was estimated in term of H_2-to-water mole ratio (n_{H_2}/n_{H_2O}) calculated using original

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Table 1. Characteristics of the TBAB, TBACl, and TBPB Studied

name	chemical formula	purity (100 w)	CAS RNs[a]	T_m/K
TBAB	$C_{16}H_{36}NBr$	99[b]	1643-19-2	374.15 to 378.15
TBACl	$C_{16}H_{36}NClH_2O$	97[b]	88641-55-8	
TBPB	$C_{16}H_{36}PBr$	98[b]	3115-68-2	

[a] Numerical identifiers (CAS registry numbers) assigned by Chemical Abstract Service (CAS), a division of the American Chemical Society, to every chemical that has been described in the literature. [b] Determined by high-performance liquid chromatography, HPLC.

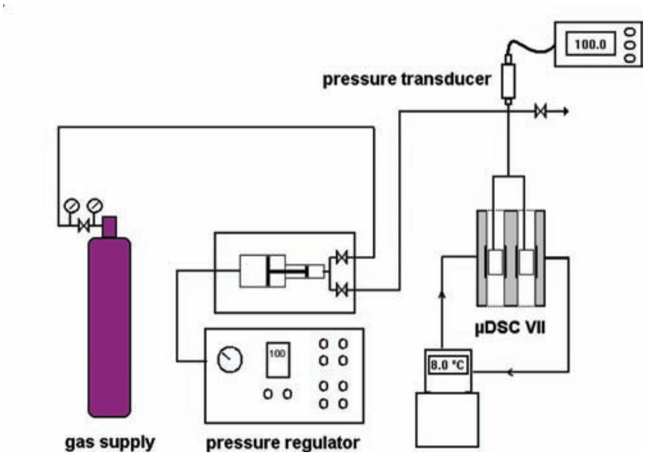

Figure 1. DSC device used to measure temperature and enthalpy of dissociation of gas hydrates.

measurements of dissociation enthalpies and (p, T) equilibrium data of the hydrogen semiclathrate hydrates. The dissociation enthalpies and phase equilibria were measured using differential scanning calorimetry (DSC) under pressure for TBAB + H_2O + H_2, TBACl + H_2O + H_2, and TBPB + H_2O + H_2 systems for the temperature range (282 to 291) K up to 31.0 MPa. Phase equilibria for binary TBAB + H_2O, TBACl + H_2O, and TBPB + H_2O semiclathrate hydrates were also measured for reference.

Materials and Apparatus

The ammonium salts (TBAB and TBACl) and the phosphonium salt (TBPB) used in this work were supplied by Fluka and Sigma-Aldrich, respectively. The characteristics and the chemical formula of these substances are given in Table 1. Here, T_m is the melting temperature. These compounds were used without further purification, and all of the data presented in the table were reported by the supplier. Freshly distilled and degassed water was used to prepare all of the solutions. The mass of the sample used was determined with an electronic mass comparator (Metler Toledo model AW205) with a precision of ± 0.01 mg. Hydrogen (H_2) was provided by Air Liquid with a certified volume fraction purity of 99.999 %.

All of the measurements were performed using DSC under pressure. The DSC device employed is represented in Figure 1. This device consisted of a Setaram micro DSC VII which can operate at temperatures between (228.15 and 393.15) K, coupled to a pressure multiplicator (supplied by Top Industry) capable to maintain a constant pressure on the sample up to 100 MPa with an uncertainty of ± 0.03 MPa. The DSC cells were designed by Setaram to work up to 40 MPa, and their volume was 0.25 mL. The pressure was measured using a pressure gauge (0 to 70) MPa Druck model PTX-7800 with an uncertainty of ± 0.20 % FS. The calibration of the DSC apparatus was performed in the temperature range (233 to 353) K using the melting of high purity of mercury, gallium, and napthtalene. Ice melting experiments were also performed to determine the uncertainty of the measured enthalpies. The uncertainties concerning the temperature and the enthalpies of dissociation measured by DSC were found to be better than ± 0.4 K and ± 0.06 kJ·mol^{-1} (H_2O), respectively.

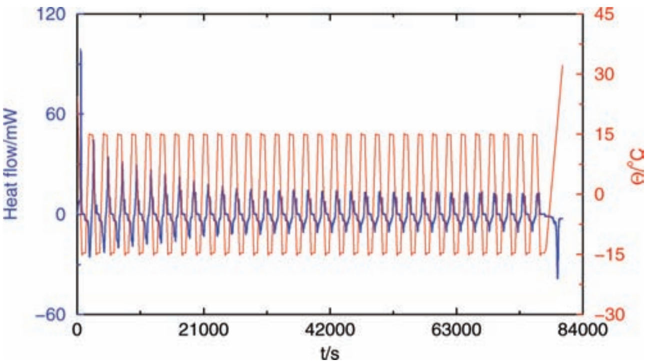

Figure 2. Heat flow delivered by TBAB (1) + H_2O (2) + H_2 (3) (w_1 = 0.400) under a pressure of 15.0 MPa during cooling−heating cycles.

Experimental Method

To measure the temperature and the enthalpy of dissociation of semiclathrate hydrates and gas + semiclathrate hydrates, samples of approximately 50 μL of solution of peralkylonium salts were subjected to a controlled static pressure of gas. Aqueous TBAB, TBACl, and TBPB solutions were prepared according to the stoichiometry showing a congruent melting point and a maximum of thermal stability at atmospheric pressure. This stoichiometry corresponds to 26[22,23] molecules of water for TBAB (1) + H_2O (2) semiclathrate hydrate (w_1 = 0.400), 29.7[24] molecules of water for TBACl (1) + H_2O (2) (w_1 = 0.342), and 32.0[24] molecules of water for TBPB (1) + H_2O (2) (w_1 = 0.371).

The kinetics of the hydrate formation process is usually increased with stirring, but the cells of the DSC device are not equipped with any stirring system. So, to accelerate the formation process, a multicycle mode of the crystallization of hydrate, described and validated in a previous paper,[25] was adopted. In this method, each cycle is composed of a cooling down to 258.15 K (scan rate 3 K·min^{-1}) followed by a heating (scan rate 3 K·min^{-1}) to a temperature lower than the temperature of dissociation of the gas + semiclathrate hydrate and higher than the dissociation temperature of the semiclathrate hydrate. The time between heating and cooling is equal to 10 min. The semiclathrate hydrate is formed and then dissociated during each cycle, while the gas + semiclathrate hydrate quantity increases during the global process. The disappearance of the semiclathrate hydrate results in a reduction of the surface of the peaks of crystallization and fusion of the semiclathrate hydrate cycle after cycle as illustrated in Figure 2. During the last cycle the mixture is then heated to the ambient temperature (scan rate 1 K·min^{-1}), and the dissociation enthalpy of the gas + semiclathrate hydrate is calculated from the surface of the last peak of DSC using a deconvolution method which allows to remove the residual amount of semiclathrate hydrate eventually not converted into gas + semiclathrate hydrate.

The molecular hydrogen uptake stored in the compounds was determined by an indirect way, in terms of H_2-to-water mole ratio (n_{H_2}/n_{H_2O}). According to previous works,[18,26] this ratio was calculated using original measurements of dis-

Table 2. Enthalpies ΔH_{diss} and Temperatures of Dissociation (T_m) of H_2 + TBAB, TBACl, or TBPB Semiclathrate Hydrates for Different Gas Pressures

$\frac{p}{MPa}$	$\frac{T_m}{K}$	$\frac{\Delta H_{diss}\ (H_2O)}{J \cdot g^{-1}}$
	TBAB + $26.0H_2O$	
"0.00"[a]	284.8	324.30
12.9	286.5	324.74
19.7	286.9	326.61
24.4	287.2	326.84
	TBACl + $29.7H_2O$	
"0.00"[a]	287.4	329.76
14.9	288.9	332.99
25.0	289.1	333.92
30.1	290.1	334.13
	TBPB + $32.0H_2O$	
"0.00"[a]	280.6	316.79
12.1	285.0	318.39
18.2	286.5	318.78
23.3	287.2	318.98

[a] "0.00" means no gas added and measurement done under air at atmospheric pressure.

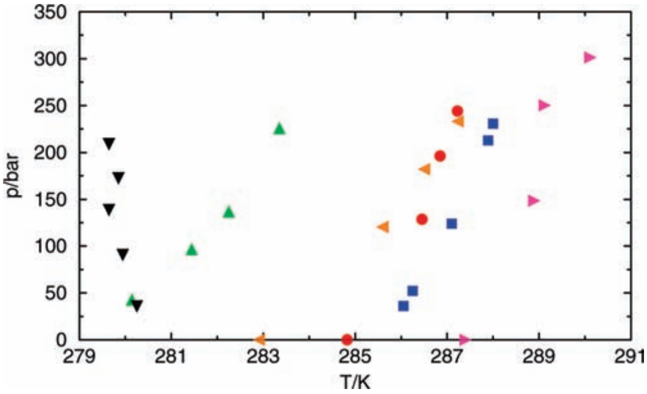

Figure 3. (p, T) data for additive + water + H_2 systems: ●, TBAB (1) + H_2O (2) + H_2 (3), w_1 = 0.400 measured in this work; ■, TBAB (1) + H_2O (2) + H_2 (3), w_1 = 0.430 from Arjmandi et al.;[16] ▲, TBAB (1) + H_2O (2) + H_2 (3), w_1 = 0.100 from Arjmandi et al.;[16] ▼, TBAB (1) + H_2O (2) (without gas), w_1 = 0.100 from Arjmandi et al.;[16] right-pointing triangle, TBACl (1) + H_2O (2) + H_2 (3), w_1 = 0.342 (this work); left-pointing triangle, TBPB (1) + H_2O (2) + H_2 (3), w_1 = 0.371 (this work).

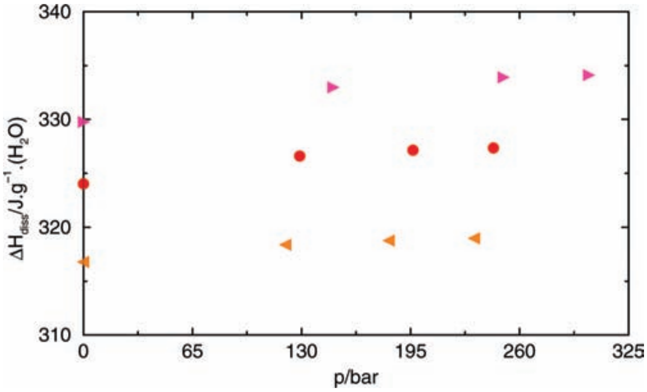

Figure 4. Enthalpies of solid to liquid + vapor phase change, ΔH_{diss}, measured by DSC for different additive + water + H_2 systems at various pressure of hydrogen; ●, TBAB (1) + H_2O (2) + H_2 (3), w_1 = 0.399 measured in this work; right-pointing triangle, TBACl (1) + H_2O (2) + H_2 (3), w_1 = 0.342 (this work); left-pointing triangle, TBPB (1) + H_2O (2) + H_2 (3), w_1 = 0.371 (this work).

sociation enthalpies and (p, T) equilibrium data of the H_2 + semiclathrate hydrates.

The hydrogen uptake into semiclathrate (n_{H_2}/n_{H_2O}) which characterizes the hydrogen-to-water mole ratio was determined as:[18,26]

$$\frac{n_{H_2}}{n_{H_2O}} = \frac{\Delta h_d(\mathrm{kJ} \cdot \mathrm{mol_{H_2O}}^{-1})}{\Delta h'_d(\mathrm{kJ} \cdot \mathrm{mol_{H_2}}^{-1})} \tag{1}$$

where Δh_d is the dissociation enthalpy directly measured by DSC in $J \cdot g^{-1}$ of solution and expressed in $kJ \cdot mol^{-1}$ (H_2O) and $\Delta h'_d$ the dissociation enthalpy expressed in $kJ \cdot mol^{-1}$ (H_2) and calculated as pointed out by Sloan and Fleyfel,[27] using the Clausius−Clapeyron equation defined as:

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta h'_d}{ZR} \tag{2}$$

where Z is the compressibility factor calculated using the virial equation of state; virial coefficients of hydrogen were taken from the National Physical Laboratory[28] (NPL). This equation is a simplification of the Clapeyron equation where only the gas phase is considered and the amount of dissolved gas is neglected.

Results and Discussion

The measured temperatures and enthalpies of dissociation of H_2 + TBAB, H_2 + TBACl, and H_2 + TBPB semiclathrate hydrates are listed in Table 2. These dissociation temperatures are represented as a function of the pressure in Figure 3. The dissociation is associated to an endothermal phenomenon, and the measured values for the H_2 + TBAB system are compared to experimental data taken from literature.[16] TBAB + H_2O phase boundaries are also shown for reference, and the presence of hydrogen into semiclathrates is confirmed by the obvious shift in the clathrate stability region (higher temperatures). This figure shows also that the presence of a peralkylonium salts promotes thermal and low pressure stability compared to H_2 (200 MPa at ambient temperature)[2,15] and H_2 + tetrahydrofuran (THF) (100 MPa at 293 K)[12] clathrate hydrates. In addition the thermal stability of the H_2 + TBACl and H_2 + TBPB semiclathrate hydrates is higher and comparable than that of the H_2 + TBAB system, respectively. However, the thermal stabilities of these systems are lower than that of the H_2 + TBAF system (dissociation temperature of the H_2O + TBAF semiclathrate hydrates ≈ 300 K at atmospheric pressure),[15] but TBAF is toxic and corrosive, while TBACl and TBPB are only irritants. Concerning TBAB, this salt is harmful.

The dissociation enthalpies of the H_2 + TBAB, H_2 + TBACl, and H_2 + TBPB semiclathrate hydrates are represented as a function of the pressure in Figure 4. As shown in Figure 3, the H_2 + TBACl semiclathrate hydrate is the most stable, and as shown in Figure 4, its dissociation enthalpy is higher than that of the H_2 + TBAB system. The H_2 + TBPB semiclathrate hydrate has a dissociation enthalpy slightly lower but comparable to that of H_2 + TBAB system.

The molecular hydrogen uptakes (n_{H_2}/n_{H_2O}) stored in the three hydrogen semiclathrate hydrates were calculated at a pressure around 15.0 MPa and are listed in Table 3. The uncertainty concerning the enthalpy per mole of hydrogen ($\Delta h'_d$) resulting from the Clausius−Clapeyron approximation was evaluated assuming that the main source of error resides in neglecting the effect of dissolved hydrogen on the gas phase volume. The error can be particularly high when the hydrogen content in the semiclathrate hydrate is close to its

Table 3. Molecular Hydrogen Uptake (n_{H_2}/n_{H_2O}) Stored in H_2 + TBAB, TBACl, or TBPB Semiclathrate Hydrates for Different Gas Pressures

p / MPa	T_m / K	Δh_d (H_2O) / $kJ \cdot mol^{-1}$	$\Delta h'_d$ (H_2) / $kJ \cdot mol^{-1}$	$(n_{H_2}/n_{H_2O})/10^{-3}$
		TBAB + $26.0H_2O$		
12.9	286.5	5.845	645.7	9.05
		TBACl + $29.7H_2O$		
14.9	288.9	5.993	353.4	17.0
		TBPB + $32.0H_2O$		
12.1	285.0	5.731	297.6	19.3

solubility in the liquid phase. Unfortunately the difficulty in the present case is that there are no data concerning the influence of ammonium and phosphonium salts on the solubility of hydrogen or on the density of H_2-saturated salt solutions, and we have then considered the solubility of hydrogen in pure water which is approximately $x_{H_2} \approx 0.0018$[29] at 287 K and 15.0 MPa. The uncertainty associated to the dissociation enthalpy ($\Delta h'_d$) obtained from (p, T) equilibrium data using the Clausius−Clapeyron approximation was evaluated at ± 20 % for TBAB and ± 11 % for TBACl and TBPB. The resulting uncertainty on the mole ratio (n_{H_2}/n_{H_2O}) was then determined according to the method described by Skoog et al.[30] by the propagation of errors in eq 1 and evaluated at ± 21 % for TBAB and ± 12 % for TBACl and TBPB. In the temperature range (282 to 291) K and at a pressure around 15.0 MPa, the value of (n_{H_2}/n_{H_2O}) is 0.0091 for the H_2 + TBAB semiclathrate hydrate, 0.017 for H_2 + TBACl, and 0.019 for H_2 + TBPB. In spite of the imprecision of the method used, these results show that the amount of hydrogen that can be stored in H_2 + TBACl and H_2 + TBPB semiclathrate hydrates is approximately two times higher than that in the H_2 + TBAB system. The quantity stored in the H_2 + THF system is already known to be eight times lower (in volume fraction at 1 MPa and 283 K) than the content stored in H_2 + TBAB semiclathrate hydrate.[15] In terms of mass fraction deduced from the ratio (n_{H_2}/n_{H_2O}), H_2 + TBACl and H_2 + TBPB semiclathrate hydrates can store 0.12 % and 0.14 % of hydrogen, respectively. Unfortunelately this amount stored is too small to be compared to the US Department of Energy (DOE) target of 0.09 mass fraction of hydrogen required for 2015.[31]

Conclusion

As a conclusion, we have measured some original calorimetric and phase equilibrium properties for hydrogen + TBAB, TBACl, or TBPB semiclathrate hydrates. This work demonstrates that the dissociation temperatures of H_2 + TBACl and H_2 + TBPB semiclathrate hydrates are very close to ambient at low pressures around 15.0 MPa. H_2 + TBACl and H_2 + TBPB semiclathrate hydrates therefore exhibit better and comparable stability than the H_2 + TBAB system at equivalent pressure, respectively. Furthermore, these two hydrogen semiclathrate hydrates are less hazardous for the health than H_2 + TBAF and H_2 + TBAB. We also performed the indirect determination of hydrogen uptake in H_2 + TBACl and H_2 + TBPB semiclathrate hydrates from dissociation enthalpy measurements and (p, T) equilibrium data. Our results demonstrate that the amount of hydrogen that could be stored in H_2 + TBACl and H_2 + TBPB semiclathrate hydrates is twice higher than that stored in the H_2 + TBAB system.

Note Added after ASAP Publication: This paper was published on the Web on June 14, 2010. An instance of TBAF was changed to THF in the text. The revised paper was reposted on June 17, 2010.

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