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# Thermodynamic model for prediction of phase equilibria of clathrate hydrates of hydrogen with different alkanes, alkenes, alkynes, cycloalkanes or cycloalkene

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ABSTRACT

In this work, structure H hydrate phase equilibrium of hydrogen in the presence of organic promoter is predicted using a proposed thermodynamic model. The investigated promoters are various *n*-alkanes, *n*-alkenes/alkynes, and cycloalkanes/cycloalkene. The van der Waals–Platteeuw solid solution theory is used for determination of the fugacity of water in hydrate phase. Phase behavior of the hydrogen + water system is modeled using the Valerama–Patel–Teja equation of state (VPT-EoS) with non-density dependent mixing rules. Due to the lack of experimental solubility data of hydrogen in the investigated promoters, the phase equilibria of the hydrogen + promoter system is treated using the VPT-EoS-G$^E$ method consisting the UNIFAC activity model and the modified Huron–Vidal (MHV1) mixing rules. The obtained results show reasonable agreement of the predictions with the existing experimental data from the literature. Finally, the hydrogen storage capacity of the corresponding clathrate hydrates is predicted as well as the occupancies of the clathrate hydrate cavities.



## 1. Introduction

Hydrogen has attracted much attention in the past decade [1]. This non-polluting compound (compared with fossil fuels) has the potential to be used as a kind of fuel for direct combustion, a means of producing electricity in fuel cells for stationary use and transport, and a medium for storing energy. As a result, separation, storage, and transportation of hydrogen are among the alluring industrial technologies [2].

The novel techniques for the storage of hydrogen can be generally grouped in three types: compression, liquefaction, and storage in solid materials. It is possible to physically store hydrogen as either a gas or a liquid. Storage as a gas (compression) generally requires high-pressure containers [3,4] though storage of hydrogen in a liquid state needs cryogenic temperatures because the boiling point of hydrogen at one atmosphere pressure is about 20.25 K [1,3,4]. Since compression and liquefaction normally consume high amounts of energy and the operations are generally performed at high-pressure conditions [1,3,4], attention is currently focused on solid storage materials which are of high safety and high energy density (in particular volumetric density) and more energy efficiency (no compression or liquefaction). Hydrogen can be stored in the form of adsorbed gas in solid materials with good energy density by volume such as carbon nanostructures consist of carbon nanofibers (CNF) and carbon nanotubes (CNT), and metal hydrides (MH) consist of $MgH_2$, $NaAlH_4$, $LiAlH_4$, LiH, $LaNi_5H_6$, $TiFeH_2$ and palladium hydride. Most metal hydrides bind with hydrogen very strongly that high temperature (393–473 K) is required to release their hydrogen content. For reducing the amount of energy of hydrogen bonding, alloys consist of a strong hydride former and a weak one such as in $LiNH_2$, $NaBH_4$ and $LiBH_4$ can be used. For solid hydrogen storage, the industry recommends a storage capacity in the range of 4.5–6% by weight at pressure of 0.5 MPa at temperatures 353-373 K. In this method there are some conflicting results about the possibility of releasing all the hydrogen that was stored in the solid materials and energy store density [5,6]. In addition there are some limitation such as low gravimetric density, poor kinetics for absorption/desorption, expensive materials and complicated procedures for activation that these limitations can be overcome in these decades [5,6].

One potential method for hydrogen storage is the use of clathrate hydrates, or gas hydrates, [7], which has attracted significant attention in the past decade. This idea is mainly due to several advantages of clathrate hydrates for hydrogen storage: low storage space, reversibility, and safety [7–10] (it should be noted that detailed studies should be undertaken to compare the application of clathrate hydrates with other hydrogen storage methods).

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Gas hydrates are ice-like crystalline structures consist of frameworks of water molecules bounded to each other by hydrogen bonds and generate polyhedron cavities around the molecules of appropriate gases and volatile liquids [11,12]. Gas hydrates are formed normally at low temperatures and high pressures [11–14]. Different clathrate hydrate structures have been known including structures I (sI), structures II (sII), and structure H (sH) [11,12]. The common structures are denoted as sI, sII and sH. sI consists of two pentagonal dodecahedral ($5^{12}$) and six tetrakaidecahedral ($5^{12}6^2$) cavities in a unit cell, while sII includes sixteen dodecahedral and eight $5^{12}6^4$ cavities in a unit cell, and sH (discovered by Ripmeester et al. [15]) is formed from three dodecahedral, two $4^35^66^3$ and one $5^{12}6^8$ cavities in a unit cell. The guest molecules that occupy the cavities normally determine the stability of each structure [11,12].

It was believed that $H_2$ cannot be encaged in clathrate hydrate lattice because of its size, in early 1940s. However, after the idea of von Stackelberg and Müller [16] about the possibility of trapping such small molecules in sII clathrates with help of other gases [17], Lunine and Stevenson [18] proposed simple hydrogen clathrate hydrates. They also determined the double cage occupancies of hydrogen and methane in a binary mixture hydrates [17,18]. Having measured the phase equilibria of binary gas hydrates of $H_2$ + He in the presence of tetrahydrofuran (THF) and hexafluorophosphoric acid (HPF6), Udachin et al. [19] investigated the possibility of trapping one hydrogen in a small cavity at very high pressures [17].

Later, Dyadin et al. [20] and later Mao et al. [21] described the capability of clathrate hydrates to store hydrogen molecules. They found that hydrogen can be stored (trapped and stabilized) in clathrate hydrates as sII at extreme conditions (e.g. at a pressure of 200 MPa and at a temperature of 273 K) [17,18]. However, these high pressure conditions did not make the idea of storage of hydrogen in clathrate hydrates as an industrial and economical technique until the work of Florusse et al. [7], who studied the formation of hydrogen hydrate in the presence of THF at moderate pressures (about 5 MPa), which is much less than the previously reported formation pressure of $H_2$ + THF by Udachin and coworkers [17,19]. They concluded that if the large cavities of sII hydrate are occupied by tetrahydrofuran (THF), hydrogen clathrate hydrate could be stabilized at these moderate equilibrium pressures; however, this would reduce the $H_2$ storage capacity because THF molecules occupy the large cavities of the hydrate and consequently $H_2$ molecules can occupy only small cavities. After carrying out a set of experiments on $H_2$ + THF clathrate hydrate at pressure of 12 MPa and temperature of 277.3K, Lee et al. [22] claimed that if the concentration of THF in aqueous solution is between 2.0 and 5.56 mol%, the storage capacity is estimated to be 2.09 mass% of $H_2$. In this case, $H_2$ molecules can also occupy the large cavities. Furthermore, decrease of THF concentration in aqueous solution (about 0.15 mol%), leads to the maximum storage capacity of about 4 mass% of $H_2$. The details of other studies on clathrate hydrates of binary mixture of $H_2$ + THF can be found in the work of Strobel et al. [17]

Apart from THF, other hydrate formers such as propane, 2,5-dihydrofuran, 1,3-dioxolane, tetrahydropyran, cyclopentane, cyclohexanone, 1,4-dioxane have been demonstrated to form sII clathrate hydrates with hydrogen, some of them with more efficient storage conditions than those of the binary mixtures of THF + $H_2$ [10,17,23–27]. The phase behavior of clathrate hydrates of the carbon dioxide/ethane + $H_2$ systems has been also paid attention [2,28–31] to investigate the participation of $H_2$ in hydrate structures and consequently form sI with carbon dioxide/ethane.

Another possibility is to store hydrogen molecules in sH clathrate hydrate. The help gases can occupy the small and medium cavities and the large cavities of sH hydrate are occupied by promoter, in the case of using promoters like methyl tert-butyl ether, methylcyclohexane, and 1,1-dimethylcyclohexane [17]. The sH hydrogen clathrate hydrates have generally lower stability pressure than the sII clathrate hydrates of pure hydrogen. Duarte et al. [32] investigated the possibility of hydrogen storage in the sH clathrate hydrate in the presence of hydrocarbons, which are immiscible in the aqueous phase and obtained the minimum clathrate hydrate stability pressure of 60.1 MPa [33].

Semi-clathrate hydrates have been also proposed as a potential medium of hydrogen storage by Hashimoto et al. [34] in 2006. They measured the phase equilibria of the corresponding hydrates in the presence of 3.6 mol% of tetra *n*-butyl ammonium bromide (TBAB) aqueous solutions at stoichiometric ratio and observed higher stabilizing temperatures of the corresponding semi-clathrate hydrates of hydrogen + TBAB than those of clathrate hydrates of hydrogen + THF. Several experimental studies have been done later to clarify the phase equilibria of semi-clathrate hydrates of hydrogen in the presence of TBAB or TBAF aqueous solutions [35–42].

However, searching for efficient, economical, safe, industrial, and high capacity appropriate hydrate promoters and structures for hydrogen storage is still a challenge. Due to the fact that experimental measurements of the corresponding phase equilibria are generally time-consuming and costly and in order to study the industrial feasibility of clathrate hydrate storage capacity in the presence of promoters, reliable thermodynamic models are required. To the best of our knowledge, there are limited models available in open literature for this purpose. Density functional theory (DFT) [43], the integrated ab initio model [44], the molecular dynamic simulations [45], and the Monte Carlo simulations [46] are the so far proposed models to evaluate the equilibrium conditions, hydrogen storage capacity, or cage occupancy of hydrogen for hydrogen clathrate hydrates. Regarding prediction of phase equilibria of clathrate hydrates of binary mixture of $H_2$ + THF, Lee et al. [47] developed a thermodynamic model assuming double occupancy of $H_2$ within the small cavities and low pressure quadruple occupancy of $H_2$ in the large cavities in structure II. They assumed the concentration of THF in the liquid phase can lead tuning of the hydrogen storage capacity of the hydrate. There was discrepancy of the result by Lee et al. [47] with several other researchers [6,48–51]. On the contrary to what Lee et al. [47] reported, Strobel et al. [48] showed that hydrogen storage does not increase upon decreasing the THF concentration below the stoichiometric 5.6 mol% solution to 0.5 mol%, at constant pressure. The maximum amount of hydrogen stored in this binary hydrate was about 1.0 wt% at moderate pressure and is independent of the initial THF concentration over the range of conditions tested. In addition, this result was also indicated by Martin and peters [6]. They showed that at the hydrate formation conditions, THF occupancy of large cavities is nearly constant and equal to 1, being independent of the concentration of THF in the liquid phase. Their results indicate that at the pressures of hydrogen hydrate formation, the small cavities of the hydrate are singly occupied by hydrogen and that at moderate pressure; hydrogen hardly displaces the promoter from the large cavities, even when the concentration of the promoter is reduced below the stoichiometric concentration. Later, Strobel and coworkers [52] regressed the parameters for $H_2$ + THF binary mixture in the CSMGem framework [12] to predict the corresponding phase equilibria. Another attempt has been made by Martín and Peters [6] who applied the cubic-plus-association equation of state (CPA-EoS) [53] to deal with the liquid and vapor phases and the solid solution theory of van der Waals–Platteeuw (vdW–P) [54] to model the hydrate phase as sII clathrates. Another approach has been reported by Mohammadi and co-workers [55,56], who successfully studied the use of the artificial neural networks (ANNs) mathematical tool for representation/prediction of the phase equilibria of $H_2$ + THF clathrate and $H_2$ + TBAB semi-clathrate hydrates.

Perhaps, the only work for modeling the phase behavior of the sH clathrate hydrates of hydrogen + promoter systems is the