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Thermodynamic predictions of various tetrahydrofuran and hydrogen clathrate hydrates

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ABSTRACT

Tetrahydrofuran (THF) is one of the most widely used analogues for gas hydrates as well as a commonly used additive for reducing the formation pressure of a given hydrate process. Hydrates are also currently being investigated as storage materials for hydrogen as well as materials for hydrogen separations. Here we present a thermodynamic model, based on the CSMGem framework, that accurately captures the phase behavior of various hydrates containing THF and hydrogen. The model uses previously regressed parameters for components other than THF and H_2, and can reproduce hydrate formation conditions for a number of hydrates containing THF and/or hydrogen (simple THF, THF + CH_4, THF + N_2, THF + CO_2, THF + H_2, CH_4 + H_2, C_2H_6 + H_2 and C_3H_8 + H_2). The incorporation of THF and H_2 within this model framework will serve as a valuable tool for hydrate scenarios involving either of these components.

1. Introduction

Clathrate hydrates are crystalline inclusion compounds formed from hydrogen bonded water molecules that form polyhedral cavities and trap small guest molecules, typically at elevated pressure and/or low temperatures [1]. Three common structures (sI, sII and sH) are known to form, largely as a function of the size of the guest molecule [2,3]. The cubic unit cell of sI hydrate consists of six $5^{12}6^2$ cavities and two 5^{12} cavities with 46 water molecules. The nomenclature A^xB^y is used, where "*x*" and "*y*" signify the number of A- or B-sided faces that construct a polyhedral cavity, e.g. $5^{12}6^2$ indicates 12 pentagonal faces and two hexagonal faces. Simple (one type of guest) sI hydrate forms readily with molecules like methane or carbon dioxide. Larger molecules like tetrahydrofuran (THF) or propane form sII hydrate. The face centered cubic unit cell of sII hydrate contains eight $5^{12}6^4$ cavities and sixteen 5^{12} cavities with 136 water molecules.

Clathrate hydrates have a significant role in a variety of applications [4]. Significant quantities of hydrated gas exist within arctic regions and ocean sediments, representing a large potential future energy resource [1]. Also, the blockage of oil and gas pipelines caused by hydrate formation is a significant concern to the energy industry [5]. Clathrate hydrates have been investigated as storage and transportation materials for natural gases [6,7], and more recently, as possible materials for the storage of hydrogen [8,9]. Additionally, hydrates have been proposed as separation materials for gas mixtures in which one component forms hydrate phases more readily than another [10], as well as materials for CO_2 sequestration [11,12]. Finally, due to the appreciable latent heat associated with hydrate formation/dissociation, these compounds have been proposed as phase change materials for refrigeration applications [13].

The requirement of elevated pressure for gas hydrate formation provides an additional element of complexity to the study of these materials within the laboratory. Additionally, compression costs are typically one of the largest expenses for an industrial process, thus pressure reduction strategies aid process economics. The complete miscibility of THF with water and the easily attainable hydrate formation conditions (277.6 K at 1 bar) provide clear advantages compared with other gas hydrates. Thus, THF hydrate is commonly studied as a substitute for natural gas hydrates [14–17], although the transferability of THF hydrate properties to gas hydrate properties has recently come into question [18]. THF has been used as an additive to reduce the formation pressures for hydrogen storage [19], gas separation schemes [10,20], as well as refrigeration applications [13].

Clearly the thermodynamic formation conditions of hydrates containing THF and/or hydrogen are required for a separation/storage process. These conditions will dictate the number of equilibrium stages required for a separation, or the minimum pressure required for gas storage applications. Given the infinite number of compositional combinations containing THF and gas mixtures, a

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predictive thermodynamic model will enhance empirical laboratory measurements.

Previous researchers have developed models for hydrates containing THF. In 2001, de Deugd et al. [21] used a model, in which the hydrate phase chemical potential was calculated using the method of van der Waals and Platteeuw [22], that was capable of accurately predicting the formation conditions for binary hydrates of $THF + CH_4$ as well as other water soluble hydrate formers. Also in 2001, Seo et al. [23] presented a similar model which sufficiently reproduced equilibrium conditions for $THF + CH_4$ and $THF + N_2$ hydrates. In 2006, Lee et al. [24] developed a thermodynamic model for $THF + H_2$ hydrates as well as hydrocarbon + H_2 hydrates. This model assumed double occupancy of H_2 within the 5^{12} cavities and low pressure quadruple occupancy of H_2 in the $5^{12}6^4$ cavities; features that have been experimentally determined to be unreasonable [25–28].

Although these previous thermodynamic models sufficiently reproduce hydrate equilibria for their respective specific systems, the parameters used between the different models vary significantly. It would be useful to be able to predict the phase behavior of any of these given systems with a single set of consistent parameters within the framework of a single model. Additionally, all of the previous models fail to take into account the phase diagram of pure THF hydrate.

In this work we have determined parameters for THF and H_2 based upon the CSMGem framework [1]. CSMGem is a non-ideal hydrate solid solution model for multi-phase equilibria [29–32]. This model has been established to accurately predict hydrate equilibria and is currently capable of predictions for 27 hydrate forming components and their mixtures [33]. The incorporation of THF and H_2 within this framework will serve as a valuable tool for hydrate scenarios involving either of these components.

2. Model formulation

The model formulation is based on that of CSMGem. Specific details of this model have been published previously [29–33]. An overview of the model and applicable model parameters are provided as supplementary material.

3. Determination of new parameters

For a new component in the CSMGem framework, ten new parameters are required for sI and sII hydrate calculations: a_i, ε_i, σ_i, D_i, Δr_{ij} (for four cavities), κ (for two structures). The core radii a_i were determined from virial and viscosity relations [34], and the molecular diameters D_i were determined from Spartan® calculations at the Hartree–Fock level. The compressibility parameters κ for THF were assumed to be that of propane and the compressibility parameters for H_2 were assumed to that of nitrogen. The value of the repulsive constant $\Delta r_{\mathrm{THFsIIL}}$ for THF in the large cavity of sII was determined by matching lattice parameter data for THF hydrate [35] as a function of temperature; all other repulsive constants for THF are zero. Repulsive constants for hydrogen were estimated by correlating previously determined values for other guest components as a function of molecular diameter, and extrapolating to the diameter of hydrogen.

The remaining two parameters for THF and H_2, ε_i (the depth of the intermolecular potential well) and σ_i (the separation between molecular cores at zero potential), were determined by regression to experimental data. For THF, these parameters were determined by adjustment to match the experimental T–x diagram for pure THF hydrate, as well a single set of p–T data for $THF + CH_4$ hydrate with known parameters for CH_4. The two data sets were chosen to encompass a large range of temperature (270–300 K), as the Langmuir constant is a sensitive function of temperature [36]. The quality of the regressed parameters was tested by predicting the remaining $THF + CH_4$ data, as well as other binary hydrate data sets with THF and other guest molecules with known parameters. Once the parameters for THF were determined, the remaining parameters for H_2 were determined by regression to two sets for $THF + H_2$ hydrate data over a wide experimental temperature range. The quality of H_2 parameters was tested by predicting the remaining experimental $THF + H_2$ data sets, as well as H_2 + hydrocarbon data using known hydrocarbon parameters.

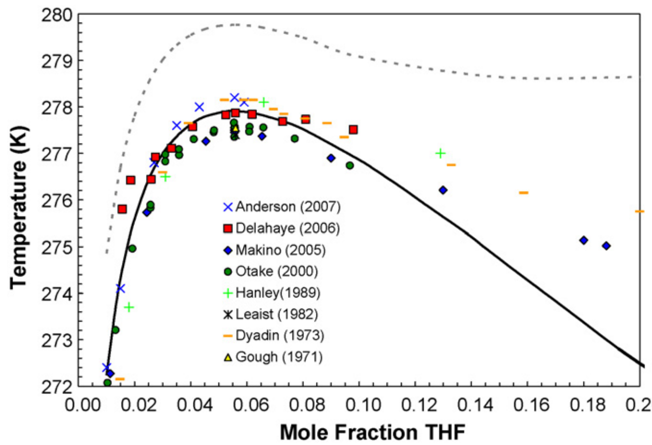

Fig. 1. T–x diagram at 1 bar for $THF + H_2O$ [13,26,37–42]. Model predictions from the current work (solid line) and Multiflash® (dashed line).

4. Model results and discussion

The phase diagram of pure THF hydrate has been studied extensively [13,26,37–42]. Fig. 1 compares data for the THF hydrate melting temperature as a function of THF composition. At the congruent melting composition, $THF \cdot 17H_2O$, the range of data reported is within about 0.8 K. As noted by Gough and Davidson in 1971 [42], the melting temperature of THF hydrate is influenced by the presence of air within the sample. The available data suggest that the congruent melting point of THF hydrate containing little or no air lies at 277.55 ± 0.1 K [42]. The most complete T–x data set for THF hydrate that accurately reproduces this value was reported by Otake et al. [38]. The set of data by Makino et al. [37] also reproduces this value; however, these data were not obtained isobarically. Together with the T–x data from Otake et al. [38] and the 5.0 mol% $THF + CH_4$ hydrate data set from de Deugd et al. [21], Kihara parameters were chosen in such a manner that the sum of the squares of fugacity differences between the hydrate and aqueous phase was minimized. The 5.0 mol% $THF + CH_4$ data set of de Deugd et al. [21] was included in the regression to obtain a larger range of temperature to regress over. Methane Kihara parameters that were previously regressed for this model were used without further adjustment (Table S6). Optimized Kihara parameters for THF are given in Table S6.

Fig. 1 shows the T–x diagram at 1 bar using the currently optimized Kihara parameters for THF. The model agrees well with the experimental data up to about 10 mol% THF, with a + 0.35 K deviation from the accepted 277.55 ± 0.1 K value for congruent THF hydrate melting point. Model predictions from the commercial software Multiflash® are shown for comparison. At THF compositions greater than 10 mol%, the model deviates to lower temperatures than the experimental data. This deviation is most likely due to inadequacies of the Van Laar liquid activity model at high THF compositions. We note that compositions above 10 mol% THF are rarely used in practice for hydrate formation as THF concentrations above ~6 mol% tend to thermodynamically inhibit hydrate formation.