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The difference between aspired and acquired hydrate volumes – A laboratory study of THF hydrate formation in dependence on initial THF: H_2O ratios

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ABSTRACT

The study reports on the differences between theoretically expected and effectively obtained volume fractions of THF hydrate depending on the THF-H_2O ratio in the initial solution against the background of using it as a substitute for natural hydrate in laboratory simulations. Besides the stoichiometric solution, initial solutions with either H_2O or THF as excess phase were prepared to define the wanted volume of hydrate in advance. In order to achieve a chemical equilibrium a complete conversion of H_2O and THF into THF hydrate and the presence of a pure excess phase is impossible. Based on the specific enthalpy of hydrate- and ice melting gained from calorimetric measurements, considerably lower than expected hydrate volumes are concluded. For the stoichiometric solution, containing 19.1 Wt% THF, enthalpy recalculations and the occurrence of an ice melting endotherm indicate incomplete conversion with a residual of 4.3 Vol% unconverted THF-H_2O solution. The deviations from expectations increase with decreasing amount of aspired THF hydrate saturation and are stronger when formed from H_2O excess solutions with up to 25 Vol% less hydrate than projected for full conversion. THF-rich solutions form hydrate with melting enthalpies that recalculate for up to 15 Vol% hydrate less than theoretical assumptions.

In samples with initial THF concentrations below 5 Wt% and above 82.7 Wt% no hydrate formation was evident.

Based on the results we propose corrections to the initial solutions when defined THF hydrate volumes are required. Furthermore, THF excess and temperatures below zero assure stable conditions for hydrate-liquid setting at atmospheric pressure.

1. Introduction

Tetrahydrofuran (C_4H_8O, THF) is a colorless organic liquid and belongs to the chemical compounds of cyclic ethers [1]. Due to its polar molecular structure it is fully H_2O-miscible. It forms a clathrate hydrate, an ice-like crystalline solid composed of a three-dimensional network of hydrogen-bonded H_2O molecules that confines THF as guest molecule in the hexakaidecahedra ($5^{12}6^4$) of structure II hydrates [2]. Since THF hydrate dissociates into H_2O and THF as liquid phase, THF hydrate it is strictly speaking defined as a liquid hydrate in contrast to a gas hydrate such as CH_4 hydrate dissociating into a gas phase and a liquid aqueous phase [3].

Despite the differences to CH_4 molecules in terms of size, polarity and hence hydrate guest characteristics, THF presents important advantages for studying hydrate characteristics via laboratory simulations. Whilst light hydrocarbons are only slightly soluble in H_2O and hydrate formation therefore requires elevated pressure, THF is well miscible with H_2O and hydrate forms already at moderate temperature and pressure conditions ($\leq$277 K and 0.1 MPa). Since it is possible to mix THF and H_2O in any proportions, a defined hydrate saturation in the sediment pore space can be well defined in advance simply by applying the relevant THF:H_2O ratio. This facilitates the synthesis of well-characterized hydrate-bearing sediment specimens and allows the reproduction of typical hydrate reservoir situations. Especially for the investigation of the influence of the degree of hydrate saturation in the pore space on geo-mechanical and geophysical properties of the sediment body, these simulations have long been used for laboratory studies.

Lee et al. investigated the suitability of THF hydrates as replacement for CH_4 hydrates for studies of hydrate bearing sediments.

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They concluded that THF hydrate – despite the differences between THF and CH_4 hydrates – can be used as substitute for CH_4 hydrate for macroscopic scale laboratory studies [4]. The effects of sediment matrix to the thermal properties of THF hydrate were observed by Rueff and Sloan [5]. The study shows no noticable changes of the hydrate characteristic when granular sediment is present. Pearson et al. used THF hydrate to perform acoustic and resistivity measurements on rock samples as analogues for natural gas hydrate deposits [6]. For the formation of the THF hydrate they used a THF-H_2O mixture with a THF-H_2O ratio of 1:18 assuming a complete hydrate saturation of the sample. With the addition of 0.05–0.1 M NaCl they varied the amount of unfrozen H_2O and affected the formation of THF hydrate. Yun et al. determined the compressional and shear wave velocities of hydrate-bearing sand. They varied the composition of the THF-H_2O mixtures to achieve hydrate saturations between 43% and 100% of the pore space [7]. In another study Yun et al. determined the mechanical properties of sand, silt, and clay containing THF hydrate [8]. In this study they only used three THF-H_2O mixtures to realize two different hydrate saturations of the pore space. Similar to the first study they combined 80.9 Wt% H_2O and 19.1 Wt% THF for 100% hydrate saturation. Samples with 50% hydrate-filled porosity were obtained by mixing either 90.6 Wt% H_2O and 9.4 Wt% THF or 42.2 Wt% H_2O and 57.8 Wt% THF. The first mixture produces H_2O in excess, the latter THF in excess. Rydzy et al. as well as Priegnitz et al. obtained different hydrate saturations with various THF-H_2O mixtures in order to study physical properties of hydrate bearing sediments as a function of hydrate saturation [9,10]. In any case, the supposed amounts of hydrates can only be formed, when all of the THF (or H_2O) will be transferred into the hydrate.

Corrections due to incomplete formation due to chemical equilibrium have not been considered. The stoichiometric composition of THF hydrate is 1THF: 17H_2O, which equals a ratio of 19.1 Wt% THF: 80.9 Wt% H_2O. However, the hydrate formation from H_2O and THF is not complete. As seen in the THF- H_2O phase diagram, THF hydrate coexists at equilibrium conditions with a liquid or solid phase that contains a defined amount of THF and H_2O [11]. In any case it is uncertain, if the equilibrium state is reached when THF hydrate is prepared for laboratory studies.

Different studies were carried out to determine the properties of THF hydrates, such as the enthalpies of decomposition and heat capacities [12,13], the stability fields of the THF-H_2O system at low pressures [14], the effect of sediments on the stability boundaries [5,15], and the molecular interactions between the THF guest molecules and the H_2O host molecules in the hydrate structure [16,17]. Also, THF hydrate has been widely investigated in terms of its kinetic and thermophysical properties [18,19,20,21]. The first data on THF hydrate arise from the PhD study of Palmer [22]. He investigated various compounds for the hydrate formation capabilitiy and published a range of THF hydrate formation temperature and phase diagrams showing the phase boundary of various mixtures of THF and H_2O. He noted that the eutectic temperature is not definitely to state, because the temperature around the eutectic is like a plateu in the range of 6–8 mol% THF without the formation of a definite turning point. Following this first work, Erva published freezing points of thirty-six different THF-H_2O mixtures at ambient pressures [23]. He observed a congruent melting of the mixture with an approximate composition of C_4H_8O. 16 H_2O (6 mol %) at 277.38 K. Adding H_2O to this composition makes a eutectic system with a eutectic melting point of 272 K and an eutectic mixture containing 0.9 mol% THF. Adding THF to this composition up to 30 mol% THF causes a system with incongruent hydrate melting above 273 K. Thorpe and Pinder obtained seventy-five melting points at concentrations between zero and 20 mol% THF by analysing the refractive index of the solutions [24]. They also observed defined breaks in the melting point curve and postulate that in a melting hydrate slurry exists a small amount of crystalline hydrate plus a certain amount of two liquid complexes corresponding to the upper and lower hydrogen bonded states.

To simulate certain hydrate saturations, defined volumes of hydrate are necessary. While 17 mol of H_2O react with 1 mol THF to the stoichiometric THF hydrate, a well calculated excess phase of either H_2O or THF is applied to get the desired experimental hydrate:liquid ratios:

$$17\,H_2O + 1\,THF \leftrightarrows 1\,THF\ hydrate$$

$$17\,(+Excess)\,H_2O + 1THF \leftrightarrows 1\,THF\ hydrate + Excess\,H_2O$$

$$17\,H_2O + 1\,(+Excess)\,THF \leftrightarrows 1\,THF\ hydrate + Excess\,THF$$

Thereby, aspects of phase equilibrium are commonly neglected. One prerequisite to reach a phase equilibrium between coexisting liquid and crystalline hydrate phases is fulfilled when there is no difference between the chemical potential in both phases. In a chemical equilibrium between the THF hydrate phase and the coexisting aqueous solution, a certain amount of THF will therefore remain in the aqueous solution and cannot be transferred into the hydrate phase. The same applies for the mixtures using THF in excess. Here, not all H_2O can be transferred into the hydrate phase but some H_2O will remain in the coexisting liquid phase. In addition, it is uncertain, if the equilibrium state is generally reached when THF hydrate is prepared for laboratory studies. Therefore, the reaction of H_2O and THF to form THF hydrate is likely incomplete even if stoichiometric ratios are used in the initial solution.

By using calorimetry we determined the amount of coexisting phases by calculating the specific heat of the components in the mixture upon warming to conclude on the amount of existing hydrate phase in the mixed system. Furthermore, we applied Raman spectroscopic measurements to determine the THF concentration in the coexisting aqueous phase and the THF-H_2O ratio in the hydrate phase depending on the THF concentration in the initial solution.

The objective of this work is to study THF- H_2O mixtures in the range from 0 to 100 Vol% of expected hydrate saturation, with respect of the degree of completeness of hydrate formation and composition of the excess THF- or H_2O-rich solution.

2. Experimental methods

2.1. Preparation of THF-H_2O mixtures of defined compositions

For the preparation of THF-H_2O-mixtures tetrahydrofuran (purity ≥ 99.9%, Carl Roth GmbH + Co. KG (Karlsruhe, Germany)) and purified deionized H_2O were used. The mixtures were prepared in glass or Teflon flasks. The standard uncertainty for the preparation process is ±0.01 Wt%.

Defining the ratio of THF and H_2O in the initial solution shall provide an accurate hydrate saturation in the final test specimen. Assuming all THF will be transferred into a hydrate phase, THF hydrate saturation of 100 Vol% is reached when 80.9 Wt% H_2O is combined with 19.1 Wt% THF by mass. Specimens with 50 Vol% hydrate-filled pore space are obtained by mixing either 90.6 Wt% H_2O and 9.4 Wt% THF (produces excess H_2O) or 42.2 Wt% H_2O and 57.8 Wt% THF (produces excess THF).

For experimental simulation utilizing defined hydrate saturations, the volumetric part of THF hydrate that occupies the pore space is of interest rather than the mass percentage. On the other hand, in our experience, sample preparation is easily and fast done by weighting the reactants into the reaction vessels. Therefore, a conversion of Wt% into Vol% is necessary to relate the THF:H_2O

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