

# The THF-Water System: Incomplete Hydrate Formation from a Calorimetric Point of View

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## Abstract

THF is a colorless organic liquid and belongs to the functional class of ethers. Due to its polar molecule structure it is fully water-miscible. At moderate temperature and pressure conditions, water and tetrahydrofuran (THF; C<sub>4</sub>H<sub>8</sub>O) form a sII type hydrate where only the large cages are occupied. As these requirements are easy to realize in the laboratory, THF hydrate is often used as surrogate for natural hydrates in laboratory experiments. Without the need of a complex pressure system, sediment structures with defined hydrate contents in the pore space can be simulated, for instance to perform experiments on the physical and mechanical behavior of hydrate-bearing sediments.

The stoichiometric composition of THF hydrate is THF : 17H<sub>2</sub>O, which equals a ratio of 19 wt% THF : 81 wt% H<sub>2</sub>O. The hydrate formation from water and THF is not complete. As seen in the THF-water phase diagram, THF hydrate coexists at equilibrium conditions with a liquid or solid phase that contains a defined amount of THF and water. However, it is uncertain, if the equilibrium state is reached when THF hydrate is prepared for laboratory studies.

As an approach to determine the degree of completeness of THF hydrate formation calorimetric analyses were performed using a DSC (Setaram BT 2.15). A wide range of THF-water mixtures was measured to evaluate the thermal properties of THF hydrate depending on its concentration in the sample. The THF hydrate concentrations in the sample were chosen between 10 vol% and 100 vol%. The volumetric fraction of THF hydrate that forms depends on the available reactants (water and THF). Therefore, the initial THF-water mixtures were chosen to be either water- or THF oversaturated and hence, limited in THF or water, respectively.

The samples were freshly prepared before each analysis and care was taken to perform handling speedily to avoid degassing of the highly volatile THF that would result in change in sample concentration. The sample was placed in an air tight sample vessel and immediately processed on the calorimetric unit.

The measurement procedure on the calorimeter included first, a rapid cooling to allow for the total crystallization of the THF-water sample to form THF hydrate and, if water is the excess reactant, ice. This is followed by slow heating with a special focus towards the temperature ranges where phase changes were expected. To obtain clear onset and offset temperatures at these phase changes (ice/THF melting and THF hydrate dissociation) and the corresponding heat flow signals, the heating rate was here set to only 0.02 K per minute.

Here, we present the results of a series of calorimetric analyses in terms of onset and offset temperatures of phase changes for ice and hydrate formation and dissociation, respectively, as well as enthalpy of fusion data for THF hydrate and the coexisting phases.

The measurement series show that the onset and offset temperatures of THF hydrate dissociation increases with increasing THF hydrate concentration in the sample. This effect was observed, regardless if the initial sample contains THF or H<sub>2</sub>O in excess. Furthermore, in the sample series with H<sub>2</sub>O excess, ice melting was observed. Contrarily to the THF hydrate dissociation, the onset and offset temperatures of ice melting decreases slightly with increasing THF hydrate content.

In our study, the measured values for the enthalpy of fusion of THF hydrate is lower than theoretically expected values. In the literature, values for the specific enthalpy of fusion of pure THF hydrate ranging from 260 to 270 J/g are stated. The analyzed enthalpy values are on average 50 J/g lower than theoretical calculations suggests. Interestingly, THF hydrate formed from an excess THF in the initial solution deviate on average only 35 J/g from theoretical values, THF hydrate formed from an excess H<sub>2</sub>O solution deviate on average 75J/g towards lower values.

The study reveals that a simple mixing of THF and water in certain ratios does not lead to an equilibrium state where the resulting THF hydrate has stoichiometric composition. The amount of THF hydrate formed differs from theoretic predictions. From a calorimetric point of view, two measures are indicative for that: (1) the enthalpy of fusion of THF hydrate is lower than expected and (2) the melting point depression of ice indicates that a certain part of THF remains in the aqueous phase and is not incorporated in the hydrate phase.

These data can be utilized to conclude on the actual amount of THF hydrate formed and the volume of THF and water that remains unconverted.

The results are relevant for the preparation of natural hydrate equivalents which likely do not reach equilibrium conditions in the course of experimental simulations and should find consideration when defined hydrate saturations are required.

All measurements have been performed in a non-pressurized system. They are therefore beneficial and easy applicable information for laboratory experiments performed at low temperatures but at ambient pressure conditions.