Kinetics of mixed gas hydrates - One step in the carbon cycle

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Introduction - gas hydrates in the global carbon cycle

Natural gas hydrates consist of a host lattice of water molecules that forms cavities which are mainly filled by hydrocarbons e.g. CH₄, C₂H₆, C₃H₈ etc. The trapped hydrocarbons are of thermogenic as well as biogenic origin.

Modern estimates of the carbon content in natural gas hydrates range between 2500 Gt and 5500 Gt [1-3]. Therefore gas hydrates are among the major temporary reservoirs of carbon.

The aim of this work is to get a closer view on the hydrate formation processes including:

- kinetic studies of the initial stages of hydrate formation according to natural conditions i.e. the use of gas mixtures similar to natural gas compositions,
- investigations of the influence of guest molecular properties and different p,TC-conditions on the rate of hydrate growth,
- the development of a kinetic model for gas hydrate formation.

Experimental techniques and results

Due to the combination of a Raman spectrometer with a confocal microscope the composition of the gas hydrate can be analyzed in a defined volume.

Questions:

- How does the composition of guest molecules of mixed gas hydrates develop during hydrate formation? Does the composition of the initial stages differ from that at equilibrium state?
- Which role do size and shape of large hydrocarbon guest molecules play during the hydrate formation process?
- For mixed gas hydrate systems methane is trapped primarily at initial stages.
- The larger hydrocarbon guest molecule is encaged step by step until equilibrium is reached.

Preliminary results:

- Mixed gas hydrate systems methane is trapped primarily at initial stages.
- The larger hydrocarbon guest molecule is encaged step by step until equilibrium is reached.

Phase diagrams: fundamental data for kinetic studies

The larger hydrocarbon guest molecule is encaged step by step until equilibrium is reached.

This figure shows that mixed gas hydrates are more stable compared to methane hydrates under the same p,TC-conditions. From this it follows that:

1. Natural environment: Mixed gas hydrates have the largest area of occurrence.
2. Laboratory experiments: The p,TC-conditions for kinetic studies have to be adapted according to thermodynamic data of mixed gas hydrates.

With the help of single crystal X-ray diffraction we could proof that n-butane is encaged in its gauche conformation in the large cavity of structure II. This explains the unexpected enlargement of such a large molecule like n-butane into structure II.

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References: