

Dissociation kinetics of CH₄ hydrate, mixed CH₄ + CO₂ hydrate and mixed SII hydrates

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Abstract

The knowledge of hydrate dissociation kinetics plays an important role for gas production from hydrates, the stability of natural gas hydrate deposits with respect to climate change and short-term low-pressure transport and storage of natural gas utilizing the self-preservation effect – all of them issues which are in general addressed in the SUGAR project. However, the mechanism of the hydrate dissociation process turned out to be not straightforward but depends on the composition of the hydrate, pressure and temperature conditions. The dissociation process of structure I (sI) CH₄ hydrate was comprehensively studied at 0.1 MPa. In this context the so-called self-preservation process was described. But little is known about the dissociation behavior at pressures below the stability limit but larger than 0.1 MPa. The same is true for information regarding the dissociation behavior of mixed hydrates. Since the dissociation process of gas hydrates in nature may occur at pressures higher than 0.1 MPa and natural gas hydrates may also contain C₁-C₆ hydrocarbons as well as CO₂, H₂S and N₂ the knowledge of the dissociation behavior under these conditions is crucial. This study presents preliminary results from time-resolved experiments regarding the dissociation of sI CH₄ hydrate and mixed sI CH₄ + CO₂ hydrate as well as mixed structure II (sII) hydrates including C₃H₈, iso-C₄H₁₀, n-C₄H₁₀ or neo-C₅H₁₂ besides CH₄. Our work focuses on the dissociation process at subzero temperatures and pressures below the stability limit of the respective hydrates. The *in situ* observation of the dissociation process was done using a high-pressure cell which is integrated into a micro-diffractometer. Therefore, continuous monitoring of the dissociation process of hydrate into ice is possible.

Experimental setup

Time-dependent PXRD measurements were performed with a low-temperature–high-pressure cell that was integrated into a Bruker AXS Discover diffractometer. The pressure cell is running with a continuous gas flow ensuring a constant composition of the gas phase during the complete experiment. The cell can be operated in a pressure range between 0.1 MPa and 4.0 MPa and in a temperature range between 253 K and 288 K. The detection of the diffracted X-rays is carried out with GADDS (General Area Detection Diffraction System), which includes a High Star area detector.

Results

Before the observation of the hydrate dissociation process was started sI CH₄ hydrate, sI CH₄ + CO₂ hydrate (gas phase composition: 10 vol% CO₂, 90 vol% CH₄) and mixed sII hydrates containing C₃H₈, iso-C₄H₁₀, n-C₄H₁₀ or neo-C₅H₁₂ besides CH₄ (gas phase composition: 2 vol% C₃-C₅, 98 vol% CH₄) were synthesized from hexagonal ice. Since the pressure cell is run with a continuous gas flow a constant composition of the gas phase is provided during the whole experiment. After a complete conversion of ice into hydrate the pressure was decreased to 50% below the stability limit at 271 K for the sI hydrates and 267 K for the sII hydrates, respectively. The dissociation process was monitored by recording continuously powder pattern of the hydrate phase.

It turned out that the dissociation of CH₄ hydrate and mixed CH₄ + CO₂ hydrate is faster compared to the mixed sII hydrates but only within the first 5 minutes. Afterwards the dissociation rate decreases and reaches a plateau at ca. 35 % residual CH₄ hydrate and ca. 60% residual CH₄ + CO₂ hydrate, respectively. This behavior suggests the occurrence of the well-known self-preservation effect.

While a constant ratio of ice and hydrate was monitored after the initial 5 minutes for the following 120 min in case of the sI hydrates such a behavior was not observed for the mixed sII hydrates. In contrast, the dissociation process of the studied sII hydrates is completely different. Under similar conditions the mixed sII hydrates completely dissociated within the same time. But the dissociation rates of the mixed sII hydrates also differ among each other suggesting a distinctive influence of the particular large guest molecule. The experiments showed that sII hydrates including n-C₄H₁₀ are already completely dissociated after 20 min. The mixed CH₄ + neo-C₅H₁₂ hydrate shows no hydrate signals after ca. 40 min. The mixed CH₄ + C₃H₈ hydrate was completely dissociated after ca. 80 min.

Finally, the mixed $\text{CH}_4 + \text{iso-C}_4\text{H}_{10}$ was completely dissociated after 120 min. The experiments have been reproduced for the sII hydrates containing C_3H_8 and $\text{iso-C}_4\text{H}_{10}$, respectively, showing the same results.

Conclusion

In this work the dissociation behavior of simple and mixed sI and mixed sII hydrates at subzero temperatures and pressures 50 % below stability limit was studied. It turned out that the sI hydrates including CH_4 or $\text{CH}_4 + \text{CO}_2$ show the well-known self-preservation effect also at pressures above 0.1 MPa while this behavior was not observed for the mixed sII hydrates. That means under similar conditions mixed sI hydrates show a self-preservation effect while mixed sII hydrates do not. This observation could not be clarified so far and will be investigated in more detail in future.

Apart from that the mixed sII hydrates did not show a homogeneous dissociation behavior but the dissociation rate depends on the large guest molecule. Since geometry and size of the studied large guest molecules differ the difference in the dissociation rate might depend on the ability of the large guest molecule to stabilize the $5^{12}6^4$ cavity. For instance, for $n\text{-C}_4\text{H}_{10}$ it was shown by Raman spectroscopy and single crystal X-ray diffraction that it is incorporated into the hydrate cage as its gauche conformer leading to a deformation of the $5^{12}6^4$ cavity. This less stabilizing ability might explain the fast dissociation rate. However, in case of the other studied sII hydrates the influence of the stabilizing ability of the large guest molecule on the dissociation kinetics is not quite clear and will be subject of further experiments.