

Formation of clathrate hydrates: An x-ray scattering study

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Abstract

Clathrate hydrates are ice-like inclusion compounds where guest molecules are embedded in a hydrogen bond water network. Hydrates have reached general interest because they are promising candidates for gas storage and as energy source. Although the formation of hydrates is well known from the thermodynamical point of view, their formation on molecular length scales is still under investigation. In general, two different models exist describing the formation process in a liquid mixture or at the water surface via hydrate precursors or a stochastic arrangement of water and guest molecules without precursors, respectively. Thus, both models predict a different local structure of the water molecules which is accessible by x-ray scattering. In the present work, the formation process is investigated for CO₂ hydrate at the water-CO₂ interface and tetrahydrofuran (THF) hydrate from a water-THF bulk mixture.

The water-CO₂ liquid-gas interface is studied at different gas pressures in- and outside the stability region of CO₂ hydrate by means of x-ray reflectivity. Here, only adsorption of a thin CO₂ layer onto the water surface is observed in accordance with adsorption and capillary wave theory while hydrate precursors or hydrate crystallites cannot be detected. In contrast, the water-CO₂ liquid-liquid interface exhibits the immediate formation of small and mobile hydrate crystallites as observed by x-ray diffraction. Altogether, a stochastic hydrate formation model without occurrence of hydrate precursors is favored at the CO₂-water interface.

The formation of THF hydrate is studied by x-ray Raman scattering (XRS) of the oxygen K-edge and Compton scattering which are in particular sensitive to changes of the sample's local structure. By comparing XRS and Compton spectra of the supercooled liquid mixture under hydrate formation conditions at $T = 275$ K with spectra of the mixture at room temperature, no significant deviations from the expected temperature effect on the inter- and intramolecular bonds are found. This result suggests no signature of hydrate precursors which is supported by molecular dynamics simulations and DFT calculations. Hence, similar to CO₂ hydrate, a stochastic formation model is favored for THF hydrate. Furthermore, XRS and Compton spectra show large differences for THF hydrate between 253 K and the dissociation temperature of 277 K. This observation can be connected to a decrease of structural order at higher temperatures, possibly due to a break-up of the hydrate structure. At temperatures between 93 K and 253 K the measured Compton spectra differ only slightly in agreement with the bare temperature effect on the bond geometry. The configurational heat capacity extracted from the Compton profiles is constant below 253 K and increases rapidly for higher temperatures which evidences the structural rearrangement of THF hydrate.