



Experiment title:

Hydrate formation at the CO₂-water and silicon-CO₂ saturated water interface studied by high energy x-ray reflectivity

Experiment number:

SI-1505

Beamline:

ID15 A

Date of experiment:

from: 12/06/2007 to: 17/06/2007

Date of report:

19/03/2009

Shifts:

16

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Report:

Gas Hydrates are cage like structures where a guest molecule is enclosed into a hydrogen bond water network [1]. These structures are very common in nature, e.g. methane hydrates in ocean floor or permafrost regions. Hydrates are promising candidates for future energy recovery and for hydrogen storage [2]. At low temperatures and high pressures CO₂ forms the cubic structure I (sI) hydrate with a lattice constant of approximately 1.2 nm. At 0 °C the minimum pressure for stable CO₂ hydrates is 12.5 bar.

The microscopic formation process of hydrates is still not understood. Three different theories for this process are proposed in the literature: The cluster nucleation theory [3], the local structuring hypothesis [4] and a surface driven model [5]. Within the latter theory the formation at the water surface is preferred because of the higher concentration of gas molecule. Unstable cage fragments are formed and were occupied by the gas molecules which stabilize the cages and nucleation sets in. The cluster nucleation theory predicts a formation of cage fragments when gas is solved in water. After an induction time depending on the degree of supercooling and the type of gas molecule the clusters arrange and macroscopic amounts of hydrates are formed. The local structuring hypothesis is based on statistical processes which takes place in the bulk phase.

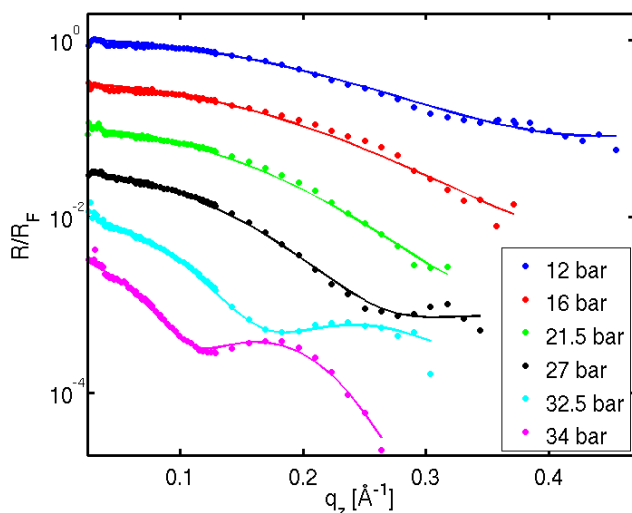


Figure 1: Sample reflectivities at different gas pressures. Solid lines represent refined curves. The curves are shifted for better visibility and normalized by Fresnel reflectivity.

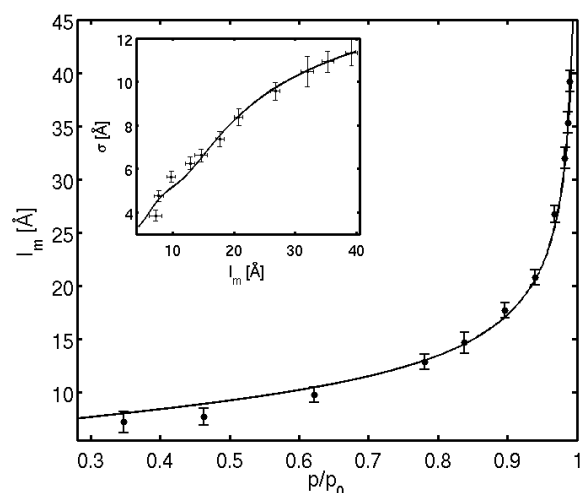


Figure 2: Adsorption isotherm. Solid line represents calculated isotherm. Inset: Roughness as function of film thickness. Line represents theory [7].

X-ray reflectivity measurements of the water-CO₂ interface provide information of the hydrate formation process at the liquid-gas interface. Due to a high solubility of CO₂ in water and short induction times of the formation process CO₂-water is an ideal system to study the hydrate formation. High energy reflectivity measurements were carried out at beamline ID15A using the new liquid surface set-up at a photon energy of 72.5 keV [6]. Such high energies are necessary because of the low x-ray transmission at higher CO₂ pressures. Reflectivities at T= 0°C and CO₂ pressures between 1 bar and just below the condensation pressure of 34.8 bar of the water-CO₂ interface were performed. A pressure dependent adsorption of CO₂ was observed (see Fig. 1 and 2) but no indications of hydrate formation was found. An adsorption isotherm [7] could be calculated with an effective Hamaker constant of $A_{eff} = (3.0 \pm 0.5) \cdot 10^{-19}$ J. Even after several hours of waiting at ambient pressures for hydrate formation or directed impurity by KBr for shorter induction times no hydrate formation became visible. After rising the pressure for condensing a macroscopic liquid CO₂ layer of several mm thickness, small hydrate clusters could be detected at the water-liquid CO₂ interface. Bragg reflexes measured at the interface occur and disappear continuously, see Fig. 3. Here further measurements are necessary to investigate the liquid-liquid interface.

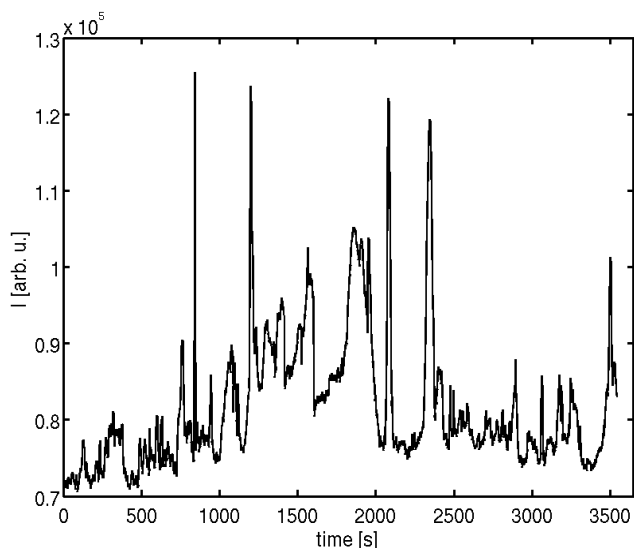


Figure 3: Timescan of the Bragg peak at $2\theta=3.027^\circ$. This is an expected peak position of a CO₂-hydrate diffraction pattern.

References:

- [1] E.D. Sloan Jr., Nature 426, 353 (2003).
- [2] H. Lee et al., Nature 434, 743 (2005).
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- [5] B. Kvamme, Annals of the New York Academy of Sciences 912, 496 (2000).
- [6] V. Honkimäki et al. J. Synch. Rad. 13, 426 (2006).
- [7] M. Paulus, C. Gutt, M. Tolan, Phys. Rev. E 72, 061601 (2006).

The results of the beamtime have recently been published in Journal of the American Chemical Society:

Felix Lehmkuhler, Michael Paulus, Christian Sternemann, Daniela Lietz, Federica Venturini, Christian Gutt, and Metin Tolan, Journal of the American Chemical Society 131, 585 (2009).