



	Experiment title: Time resolved in-situ measurements of hydrate formation at liquid - liquid interfaces	Experiment number: SI-1877
Beamline: ID15 B	Date of experiment: from: 24/06/2009 to: 30/06/2009	Date of report: 19/08/2010
Shifts: 18	Local contact(s): Dr. F. Venturini	<i>Received at ESRF:</i>
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Report:

Clathrate hydrates are ice-like inclusion compounds build up of hydrogen bonded water nano-cages in which guest molecules are embedded [1,2]. These structures are very common in nature, e.g. methane hydrates in ocean floor or permafrost regions. In recent years, hydrates reached the focus of current research because they are candidates for energy recovery and gas storage [1-4]. CO₂ hydrate in particular is discussed to be used for CO₂ storage at the ocean floor [5]. Although being subject of many studies, the formation and growth process of hydrates is still not fully understood. In a recent study, we investigated the hydrate formation process at the water-gaseous CO₂ interface by x-ray reflectivity and found a stochastic and spontaneous hydrate formation [6]. This was supported by x-ray diffraction measurements at the liquid-liquid interface with a time resolution of minutes showing the formation of small mobile hydrate crystallites. Due to the poor time resolution, it was impossible to analyze the formation dynamics in detail. Therefore, the measurement was expanded to a time resolution on the order of seconds and other interfaces within this experiment.

Hydrate formation was investigated at the liquid-liquid interfaces water-CO₂ and water-propane, and the liquid-gas interface water-xenon. For CO₂ a pressure of $p_{\text{CO}_2} > 36$ bar and for propane a pressure of $p_{\text{prop}} > 4.8$ bar was applied to condense a macroscopic liquid layer onto the water surface at $T=0.5^\circ\text{C}$. To study the liquid-gas water-xenon interface, the pressure was set between 3 bar and 6 bar in several experimental runs. Since the corresponding hydrates are stable at these pressures [1], the formation of hydrate crystallites would be possible. The sample systems vary mainly in the dissolubility of the gases, while propane dissolves only weak in water, the dissolubility of CO₂ and xenon is more than one order of magnitude higher. This is usually reflected in lower induction times for hydrate formation or the amount of formed crystallites. Furthermore, owing to different molecule sizes, CO₂ and xenon form hydrate structure sI whereas propane forms structure sII [1,2]. Thus, the formation dynamics may also be influenced by different cages sizes appearing in the different hydrate structures.

The measurements were carried out at beamline ID15B utilizing the Thales Pixium 2D detector and an incident energy of 87 keV. A special high pressure sample cell with 4 mm thick aluminum windows was used with the chiller available at ID15B. The beam size was chosen to 0.1 x 0.3 (v x h) mm². The temperature was set to $T=0.5^\circ\text{C}$ in order to avoid the

formation of ice. After the cell had been half-filled with water, it was closed and pressurized with the corresponding gas. The position of the interface was determined by a height scan utilizing a diode placed behind the sample cell before and after the gas was filled. Afterwards, the diode was moved out of the beam and the diffraction experiment started. Usually, diffraction patterns were recorded every 4-10 seconds. In contrast to earlier experiments [7], the sample was not disturbed during the experiment in order to inhibit the formation of artificially generated nucleation seeds.

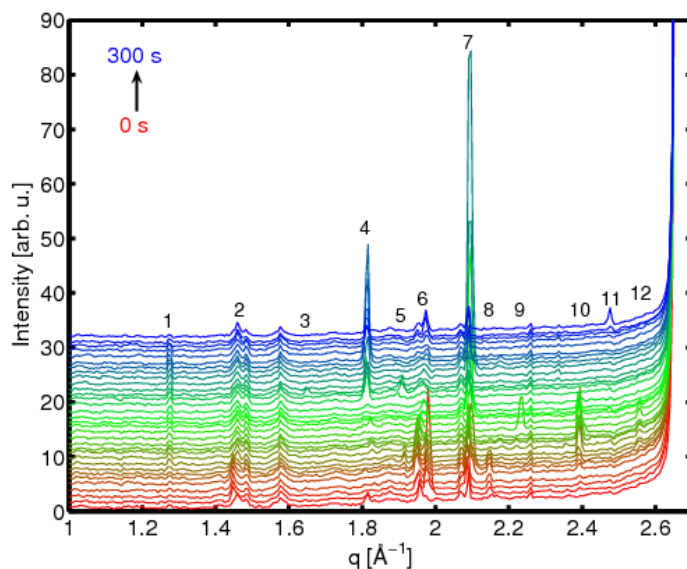


Figure 1: Consecutive diffraction patterns measured at the water-CO₂ interface. The Bragg reflection originated from hydrate are indexed. Reflections which are not marked are linked to the Al windows, in particular the strong reflection at $q > 2.6 \text{ \AA}^{-1}$.

For all sample systems, several experimental runs were performed. At the liquid-liquid water-propane interface, no formation of hydrate crystallites could be observed within approximately 4 hours. This is in line with experiments at the liquid-gas interface, where also no indication for hydrate formation was found [8]. In contrast, both CO₂ and xenon show formation of hydrate crystallites at the interface. The onset of the occurrence of Bragg reflections was distributed stochastically – from few minutes to approximately one hour. In general, this behaviour is expected for the nucleation of hydrates from supercooled liquids [1]. Unfortunately, due to the thickness of the Al windows, Bragg reflections originated from small crystallites or hydrate precursor clusters [9] are damped, so that they were not observable. Therefore, only the dynamics of the

crystallites could be studied. In Fig. 1 several consecutive diffraction patterns of an experimental run at the water-CO₂ interface are shown. 0 s marks the pattern where the first Bragg reflection was observed, the last shown pattern was measured after 300 s. The appearance and disappearance of the Bragg reflections is clearly visible. Strong reflections originated from large crystallites are usually observable for approximately 30 s up to 1 min, whereas most of the weak reflections occur only in one pattern. On the basis of these results, it can be deduced that the formation and growth of hydrates happens fully stochastically via various hydrate crystallites with different sizes. Since hydrate crystallites were found at liquid-gas interfaces in the case of xenon and the liquid-liquid interface for CO₂, and no formation was found for propane, the hydrate formation process is found to depend strongly on the type of guest molecule, in particular its disolubility in water, and the molecule size.

References:

- [1] E.D. Sloan Jr. and C.A. Koh, *Clathrate Hydrates of Natural Gases*. CRC Press, Boca Ranton, 2007.
- [2] E.D. Sloan Jr. *Nature* **426**, 353 (2003).
- [3] H. Lee et al. *Nature* **434**, 743 (2005).
- [4] T. Sugahara et al. *J. Am. Chem. Soc.* **131**, 14646 (2009).
- [5] P.G. Brewer et al. *Science* **284**, 943 (1999).
- [6] F. Lehmkuhler et al. *J. Am. Chem. Soc.* **131**, 585 (2009).
- [7] C.A. Koh et al. *J. Phys. Chem.* **100**, 6412 (1996).
- [8] M. Paulus et al. *Surf. Interface Anal.* **40**, 1226 (2008).
- [9] L.C. Jacobson et al. *J. Am. Chem. Soc.* doi: 10.1021/ja1051445 (2010).