

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



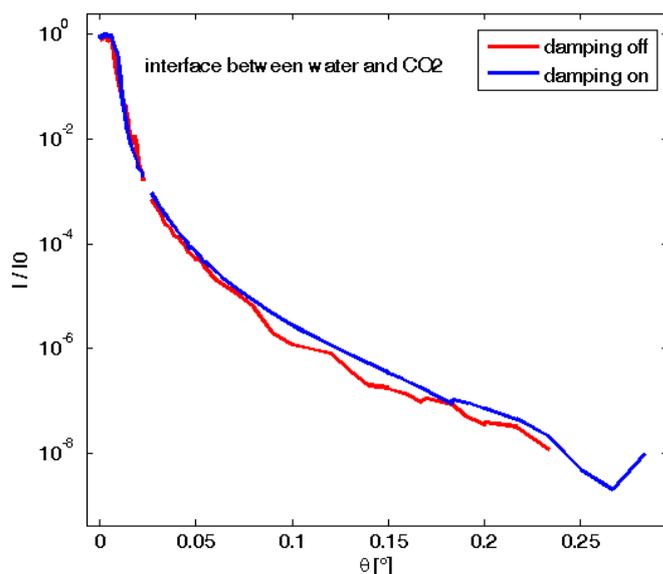
	Experiment title: Structure of the liquid-liquid water-CO ₂ interface at hydrate forming conditions –influence of inhibitors	Experiment number: SI-2362
Beamline: ID15A	Date of experiment: from: 16/11/11 to: 22/11/11	Date of report: 14/09/2012
Shifts: 18	Local contact(s): Dr. Veijo Honkimaki	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Julia Nase ^{*(1)} , Michael Paulus ⁽¹⁾ , Felix Lehmkuhler ⁽²⁾ , Sebastian Tiemeyer ^{*(1)} , Irena Kiesel ^{*(1)} , Florian Wirkert ^{*(1)} , Metin Tolan ⁽¹⁾ , (1) TU Dortmund, Physik / DELTA, Otto-Hahn-Str.4, 44227 Dortmund (2) DESY, Notkestr. 85, 22607 Hamburg		

Report:

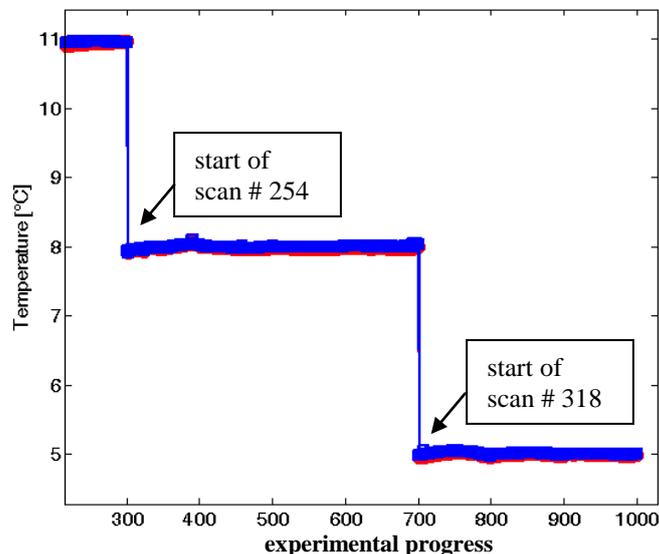
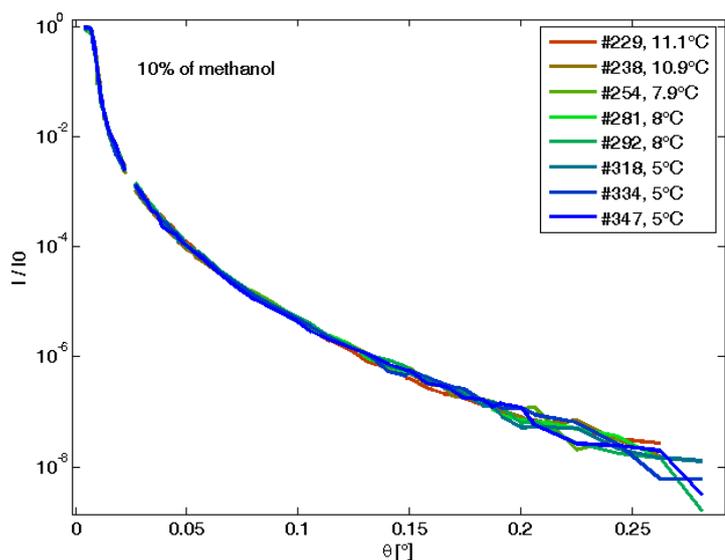
Hydrates are ice-like inclusion compounds where guest molecules are trapped in water cages. Despite their major importance in industries and fundamental research, the formation process of hydrates on molecular length scales is still not understood and currently in the focus of scientific discussion. In our recent experiment SI-2146, we studied the liquid-liquid interface between water and CO₂. We found that the interface between the two liquids can be described as a simple rough interface. This holds also when cooling the system until the region of hydrate stability is reached. However, right before hydrate is formed at the interface in the measurement cell, a thin layer was observed. This layer cannot be interpreted as a thin hydrate layer, as it is stable over ~ 40 min without provoking macroscopic hydrate growth. We concluded that CO₂ molecules accumulate in a thin region right at the interface and suggest that hydrate formation is triggered by the appearance of this supersaturated layer. It was the first time that we could directly demonstrate a change in the interfacial structure of water-CO₂ systems in the context of hydrate formation [1]. In the experiment SI-2362, we investigated how the presence of methanol, a well-known hydrate inhibitor, changes the accumulation layer.

Experiments were performed at the liquid sample setup of the high energy beamline ID15A at a photon energy of 69.9 keV. A custom made stainless steel sample cell with 2 mm thick aluminum windows and an inner radius of 12 cm was used, the same as the one in experiment SI-2164. The sample environment was able to sustain pressures up to 50 bar. The temperature was controlled via a heating foil and a water cooling circuit and monitored by two Pt100 temperature sensors. A Teflon ring in the cell provided a well-controlled meniscus of the liquid phase. We placed ~ 45 ml of a water/methanol mixture into the sample cell. The cell was then closed and flushed with CO₂. After sample alignment, a reference reflectivity curve was measured. At 11°C, the pressure was increased until the condensation pressure of CO₂ was reached and a liquid CO₂ phase condensed. The temperature was then decreased, and several reflectivity measurements were performed at each temperature step.

Using a damping table, we were able to obtain very smooth reflectivity curves and increased the quality of the curves considerably (see the Figure below).



The lower left Figure shows reflectivity curves of the interface between water/methanol (10 vol-%) and liquid CO₂. The curves are absolutely identical and do not show any temperature dependence. Hydrate formation is exothermic and leads in our measurement cell to a sudden temperature increase of about 2-3°C. It can be seen from the measurement of the cell temperature that no hydrate is formed during this series of measurements (lower right Figure).



In conclusion, the addition of methanol to the water phase inhibited the formation of CO₂ hydrate at the liquid-liquid water CO₂ interface. In that case, the reflectivity curves did not show any temperature dependence, and the curves are all exactly the same. This result confirms that an accumulation of CO₂ molecules, as we observed previously at the interface right before the formation of hydrate, does not occur when methanol as hydrate inhibitor is involved. A more detailed data analysis is currently going on.

[1] L. Boewer, J. Nase, M. Paulus, F. Lehmkuhler, S. Tiemeyer, S. Holz, D. Pontoni, and M. Tolan. On the Spontaneous Formation of Clathrate Hydrates at Water-Guest Interfaces. *J Phys Chem C*, 116(12), 8548–8553, 2012.