

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: Reflectivity study of adsorption in sub- and supercritical liquid-gas systems	Experiment number: SI-2258
Beamline: ID15A	Date of experiment: from: 15/06/11 to: 21/06/11	Date of report: 29/02/2012
Shifts: 18	Local contact(s): Dr. Diego Pontoni	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Julia Nase^{*(1)}, Felix Lehmkuhler^{*(2)}, Metin Tolan⁽¹⁾, Michael Paulus⁽¹⁾, Christian Sternemann^{*(1)}, Sebastian Tiemeyer^{*(1)}, Andre Steffen^{*(1)}, Sebastian Holz^{*(1)}

(1) TU Dortmund, Physik / DELTA, Otto-Hahn-Str.4, 44227 Dortmund

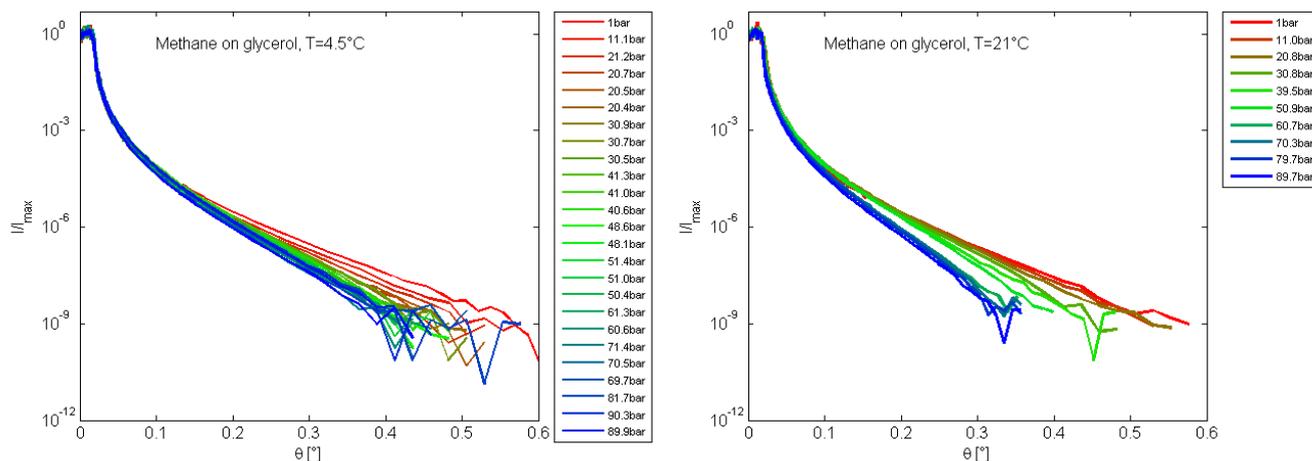
(2) DESY, Notkestr. 85, 22607 Hamburg

Report:

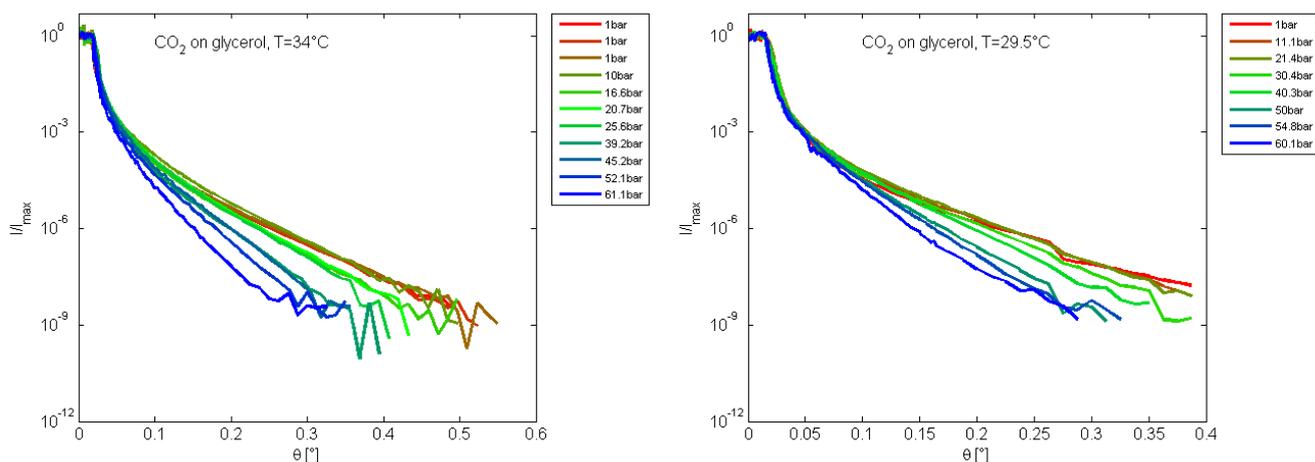
Adsorption at interfaces is critical for many processes in nature, e. g. formation of gas hydrates, catalysis, enzymatic reactions, or industrial applications. The formation of an adsorption layer enhances the gas offer significantly and is thus of importance for transport and exchange processes at membranes and interfaces in nature. Supercritical adsorption, however, is far less understood, though this phenomenon has been known for some time now and has tremendous importance in industrial applications like high pressure gas storage systems, Supercritical Fluid Chromatography (SFC), and polymer processing. In the last years, interfaces have also been investigated with regard to their relevance to hydrate formation. The differentiation between effects originating from hydrate formation and adsorption is of high importance, and the role of supercritical gases in this context remains unclear.

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 10 cm was used, similar to the one in experiment SI-2164. The sample environment was able to sustain pressures up to 100 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 ~ 25 ml of ultrapure water or glycerol into the sample cell. The cell was then closed and flushed with CO₂ or methane. After sample alignment, a reference reflectivity curve was measured. The pressure was increased in steps between 1 bar and 10 bar and a reflectivity measurement was performed at each pressure step.

The structure of glycerol and water surfaces in the presence of CO₂ and methane was investigated at various pressures. Different reflectivity series were recorded. The glycerol – methane system was studied at 4.5°C and 21°C, up to pressures of about 90 bar. The graphs below show that the structure of the interface is visibly modified with increasing methane pressure. Even if methane is in a supercritical state, a (thin) layer formation can be observed with increasing pressure.



The glycerol – CO₂ systems, measured at temperatures of 29.5°C (below the critical temperature) and 34°C (above the critical temperature), is shown in the graphs below. The applied pressure of the gas phase was limited by the bottle pressure of 60 bar. At 29.5°C, CO₂ is subcritical and thus the formation of a thin adsorption layer was expected and observed, see Figure below. The resulting reflectivity curves look similar at both temperatures. The latter two data subsets show more scatter than the methane data. This scattering is owed to the decreased glycerol viscosity at 30°C and thus increased sensitivity to vibrations, see also the discussion below.



A more detailed data analysis is going on, determining the exact shape of the interface including roughness and layer thickness of these systems. As a preliminary result, a layer formation at the liquid surface can be observed even in the case of supercritical gases.

We also measured reflectivity curves at the water – gas interface for both gases (not shown). Qualitatively, the curves show the same trends as in the graphs above. However, these data sets are harder to analyze. The viscosity of water is significantly lower than the viscosity of glycerol, so that the system is more sensitive to vibrations. The water data sets show strong scattering, which we attribute to vibrations from the nearby highway. We resolved the vibration problem in the subsequent beamtime (November 2011) by using a damping table. In that way, we obtained very smooth curves, comparable to the glycerol system at lower temperatures.

In conclusion, we observed a modification of the interfacial structure of the glycerol – methane interface with increasing pressure in the supercritical phase. A thin layer was adsorbed to the glycerol phase. The use of a glycerol substrate eliminates the possibility of hydrate formation, so that a possible formation of hydrate clusters is excluded. We should also mention that we did not observe hydrate formation with the water substrate at conditions of hydrate stability. A more detailed data treatment is going on and will reveal the exact pressure dependencies of the layer electron density profile in the supercritical state.