Report on experiments performed at ID10B #SI-1911 on the study of capillary condensation of CO2 in mesoporous materials

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X-ray reflectivity experiments were conducted on highly organized silica thin films templated by CTAB (Cetyl TrimétylAmonium Bromide) surfactant at a concentration corresponding to the formation of a 3D hexagonal phase. The objective of this experiment was to follow the capillary condensation of CO_2 inside the mesopores of this structure. Let us recall that for doing such an experiment it is necessary to expose the film to a CO_2 atmosphere the pressure of which could be varied from 0 bars to 100 bars. The challenge in such an experiment is therefore to have a specific cell in which thin films can be exposed to CO_2 under pressure in the aforementioned range of pressure. Given the pressure range and the volume of the cell necessary to conduct such experiments it is compulsory to use strong enough windows to sustain the pressure. Such windows are made of single crystal diamonds 5x5mm2 wide so that the only way to carry out the experiment is to work at high energy (here 22keV).
The first part of this experiment was used to calibrate the cell in pressure against known value of the CO2 database of NIST to find out at which pressure the gas to liquid phase transition occurs. This was done by measuring the attenuation of the x-ray beam through the cell when the pressure was progressively increased. A shown in Fig1. we can see that the transmitted intensity through the cell drops drastically when CO_2 goes from the gas phase to the liquid one. This can be measured at each temperature. For instance the measurements were made at 21.5°C and were compatible more or less with the NIST database at 22.3°C. This clearly showed that our cell was slightly offset in temperature.

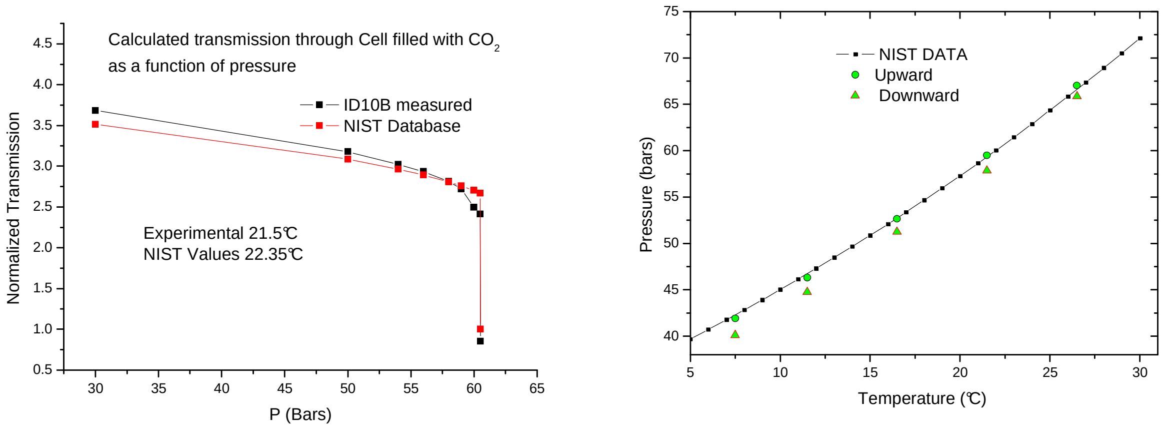

Figure 1 : left panel the transmitted intensity in the cell versus pressure ; right panel the location of the gas-liquid phase transition from the measured transmission shown in the left panel.

These measurements were made at several temperatures and compared to the “Rosée Curve” established by NIST. One can see on the right panel of Fig. 1 that we were able to calibrate fairly well our cell. This took us at least 2 shifts for sorting out the right procedure of calibration and the right set-up of the experiment. Given this calibration we were able to start the condensation experiment.

The first part of the condensation experiment was devoted to the condensation of CO_2 on a flat Silicon wafer. We spend 5 shifts to carry out such measurements without success mainly because we had a contamination of the silicon surface which seemed to give us reproducible results. We lost some appreciable beam time in this experiment which was carried out as reference experiment before measuring the capillary condensation of CO_2 in a porous material.
The end of this run was spent to carry out condensation experiments on porous films. We measured the isotherms at different temperatures on these films. We faced some problems with the too high brilliance of the beam which was destroying the sample. This was circumvented by reducing the beam size to 100µm and by shifting the beam location at each measurements. By doing so we were able to get reliable results.
As shown in Figure 2, one can see that the x-ray reflectivity curve of the film at ambient pressure

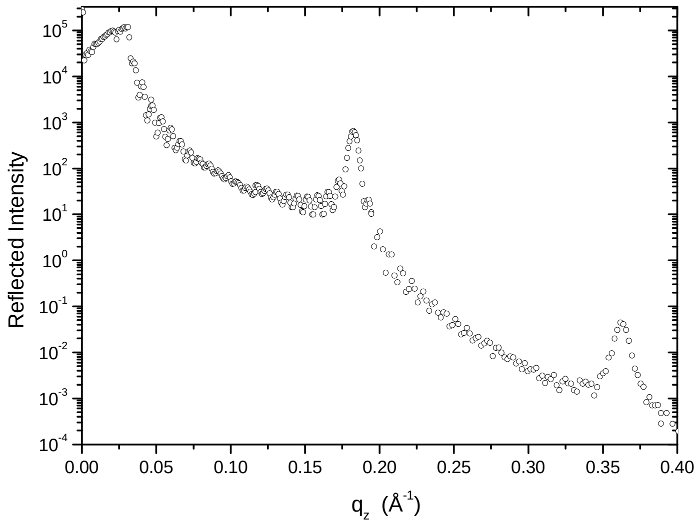

Figure 2 : X-ray reflectivity curve of the mesoporous film

The condensation was monitored by measuring both the evolution of the intensity and location of the first Bragg peak as a function of pressure at different temperatures. Given the amount of time left we were able to measure 2 cycles at 2 different temperatures.
As shown in figure 3 one can see that the peak intensity of the first Bragg peak drops when the temperature increases and simultaneously the peak shifts towards low q wave vector transfer as soon as the film is exposed to CO_2.

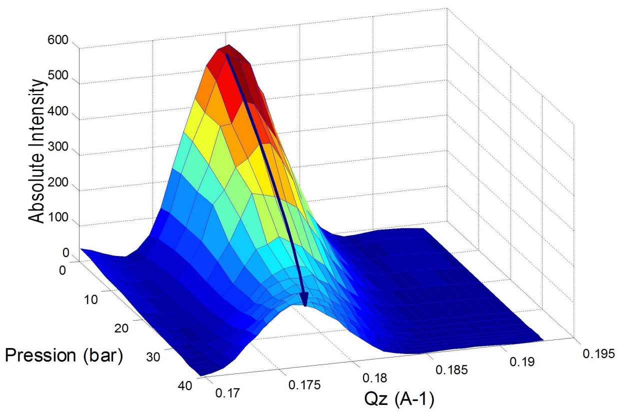

Figure 3 : Evolution of the first Bragg peak intensity versus pressure

The intensity of the 1rst Bragg peak is plotted versus pressure in Fig. 4. It can be seen that it decreases smoothly before a drastic drop when the gas transforms into liquid inside the cell. The drop in intensity is consistent with the progressive uptake of CO2 inside the film while the shift is a clear signature of the swelling of the film. Compared to what is observed in the capillary condensation of water in the same film the story is quite different. Indeed when such a film is exposed to water the capillary condensation occurs suddenly as soon as the Kelvin equation is satisfied (i.e. around p/pc =0.46 for pores of diameter 3.5nm). The continuous drop in intensity with CO2 shows that the gas continuously penetrates inside the film. This is quite unexpected and we do not yet understand the full reason for such a behavior. We would have expected an important drop of the intensity at high value of p/psat due to the very low surface tension of CO2 with materials. Indeeed water surface tension is about 7010^{-3}N/m while the one of CO2 is 410^{-3}N/m at 6°C. Therefore one can expect that the condensation occurs very close to the gas/liquid transition at p/psat=0.95. This is not the case. Note that the jump at p/psat=1 occurs due to the fact that the cell is filled with liquid CO_2.

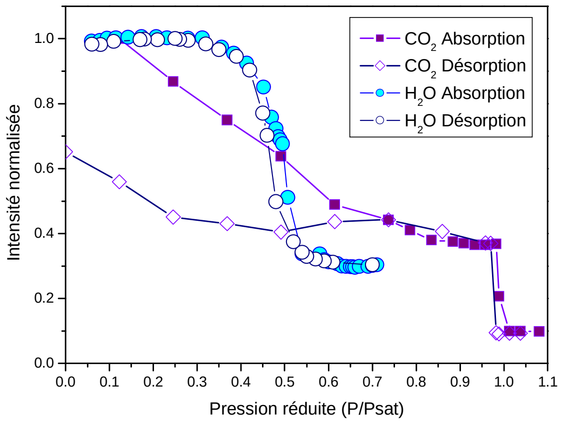

Figure 4 : comparison of the condensation of water and CO2 in the same film as deduced from the intensity of the first Bragg peak.

The above measurements have been reported in the following manifestations:

Muriel Mattenet, Karim Lhoste , Oleg Konovalov , Safall Fall , Bruno Pattier and Alain Gibaud "An X-Ray Thermo-Pressure Cell For Carbon Dioxide." SRI-2009 Proceedings Melbourne . (2009)

Etude par réflectivité des rayons X de la condensation capillaire de fluides dans des films minces mésoporeux de silice, A. Gibaud[a], S. Fall[a], M. Mattenet[b] et O. Konovalov[b], to appear in the proceedings of the Matériaux 2010, Nantes Octobre 2010

Etude par réflectivité des rayons X de la condensation capillaire de fluides dans des films minces mésoporeux de silice, Réunion du groupement Français adsorption sur des surfaces hétérogènes, Juin 2010, INSP