Experimental report

16/09/2019

Proposal: 6-02-591 **Council:** 10/2018

Title: Structure of supercritical CO2 between 30 and 70°C for pressure between 70 and 180 bar

Research area: Materials

This proposal is a new proposal

Main proposer: François SAINT ANTONIN

Experimental team: Gabriel Julio CUELLO
François SAINT ANTONIN
Gerard GEBEL
Olivier BLANCHOT
Olivier LEBAIGUE

Local contacts: Viviana CRISTIGLIO
Gabriel Julio CUELLO

Samples: Carbon dioxide

Instrument	Requested days	Allocated days	From	To
D4	7	0		
D11	3	0		
D16	4	4	18/07/2019	22/07/2019

Abstract:

SuperCritical fluids based on CO2 have become increasingly used in many industrial sectors as they can be employed for extraction, impregnation of solids inorganic), particle coating, foaming, textile and paper dyeing,…
Even the properties of the SC-CO2 such as compressibility, heat capacity, viscosity, thermal conductivity, are well known, its structural features remain very scarce for temperature between 30 and 70°C under pressure between 70 and 180 bar (corresponding to the region, roughly, just above the critical point).
Several properties in that temperature-pressure region could be explained referring to a description based on a 'gas+liquid emulsion structure';.
The goal of the project is to:
- characterised this 'gas+liquid emulsion structure' through the acquisition of systematic data in the P-T region mentioned above,
- to define the size and relative proportion of gas and liquid domains and to evaluate the mean distance within the gas and the liquid domains,
- and then, to define a relation linking the portion and the relative size of the gas and liquid domains in the CO2 supercritical state as a function of temperature and pressure.

Report about: "*Structure of supercritical CO_2 between 30 and 70°C for pressure between 70 and 180 bar*"

Initial proposers:	François Saint-Antonin	francois.saint-antonin@cea.fr
	Olivier Poncelet	olivier.poncelet@cea.fr
Co-experimentators:	Olivier Lebaigue	olivier.lebaigue@cea.fr
	Gérard Gébel	gerard.gebel@cea.fr
ILL co-proposer and Local contact:	Gabriel Cuello	cuello@ill.fr
	Viviana Cristiglio	cristiglio@ill.eu

Goal of the proposal

The goal of the experiments was to gain data for a description of the supercritical CO_2 structure (SC-CO_2) for 70-180 bar and for 30-70°C.

In a first approach, the structure that can be deduced from properties and behaviour is that, the supercritical state might correspond to a mixture of 'vapour-like' and 'liquid-like' domains forming a sort of 'emulsion'. The size of these domains is a key issue for an appraisal of the SC-CO_2 structure.

Measurements

Due to the preparation and to the calibration of the experimental means (measurement on empty cell and so on), the time for acquisition was reduced to about 48 hours and it appears that the number of points have to be reduced from the initially planned points to acquire: 11 points were recorded (see location in figure 2).

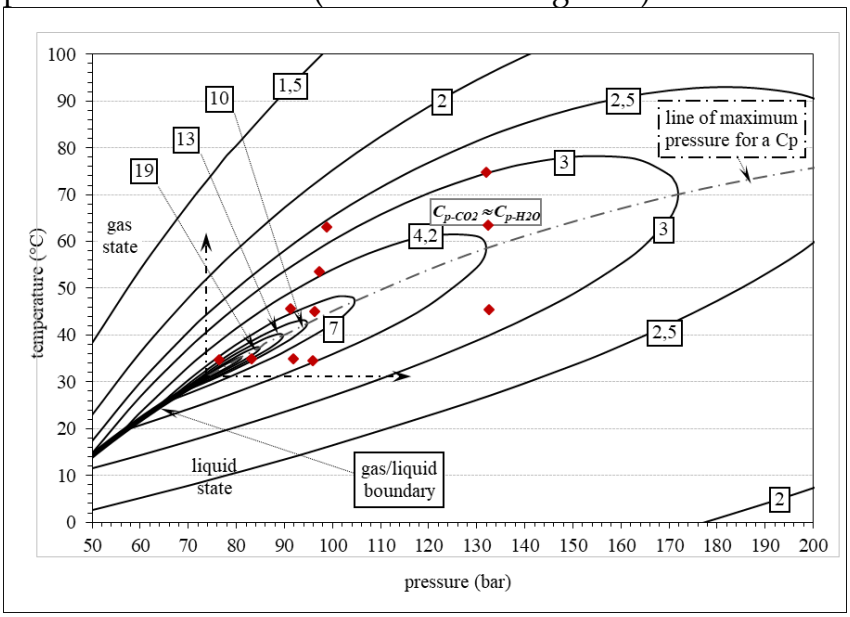

Figure 1: location of the 11 experimental points acquired (iso-Cp versus P-T map).

Results

The different curves obtained are reported in the following figures for large and small angles. The diffraction data were acquired with angle ranging from about 2° to about 120°. Even there was uncertainty about the pressure (just above the critical point), there are several differences in low and large angles from curve to curve.

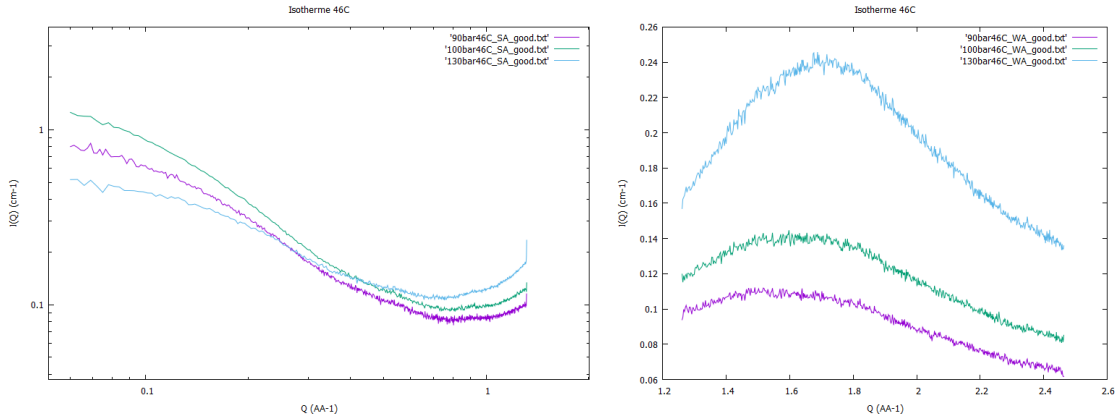

Figure 2; From ~90 to ~130 bar at about 46°C.

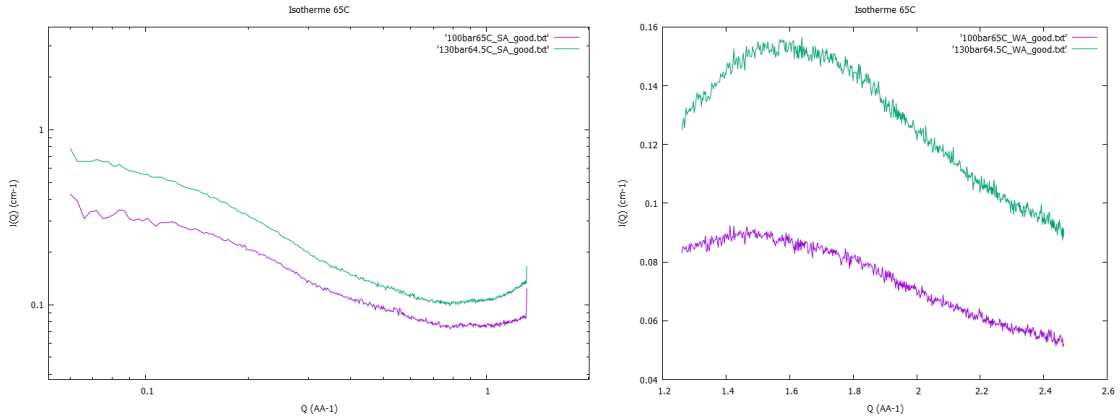

Figure 3 ; From ~100 to ~130 bar at about 65°C.

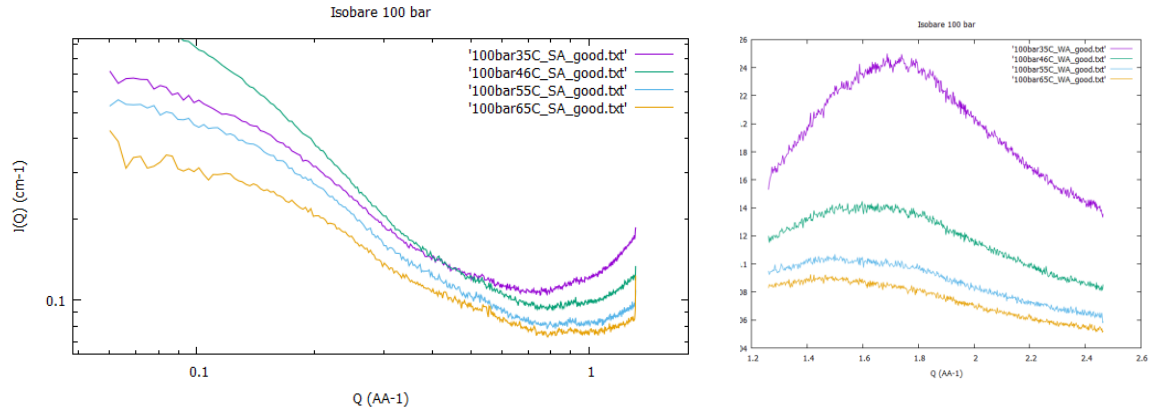

Figure 4 ; From ~35°C to ~65°C at about 100 bar.

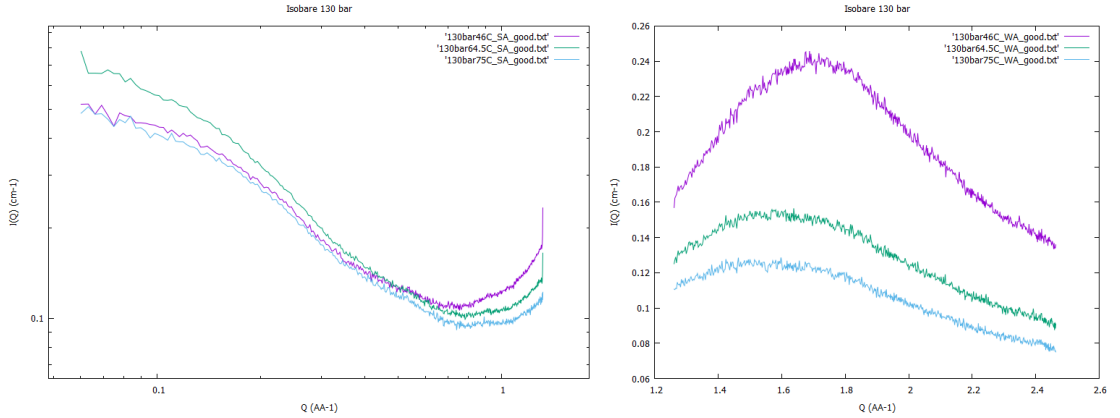

Figure 5; From ~46°C to ~75°C at about 130 bar:

Comments about the different data

The specificity of the present experiments are that both large and small angles were recorded on the same samples. The data presented on figures 9 to 12 emphasize the fact that the recorded spectra contain lot of information in each angular ranges. They exhibit a clear contribution at small angles around $Q < 0.1$ Å^{-1}. This contribution is clearly enhanced in the vicinity of the Widom line. In addition to the small-angle scattering signal, an additional oscillation is visible in the 0.4-0.5 Å^{-1}, which will be helpful to discriminate between different possible models. At large angles, a broad maximum is clearly visible and it seems to be composed of two contributions. Their relative intensity and position vary significantly depending on the experimental P and T conditions.

A thorough analysis taking in account the large variations of the specific mass of CO_2 and working on the absolute intensities is necessary to build a consistent view of the SC CO_2 structure. Indeed, simple analyses of the small-angle signal such as the presence of droplets (either gas droplets in liquid or liquid droplets in gas) with a defined size or of a density fluctuation through a Ornstein-Zernicke model do not seem to be able to reproduce correctly the data.

Moreover, it is necessary to perform a more finer analysis of the spectra (e.g. absolute signal intensity, incoherent noise, small angle deviation, …) and to check the level of coherency between large and small angle information. We are confident that valuable information will be extracted.

Conclusions

This first series of experiments dedicated to the acquisition of diffraction data for the CO_2 in the supercritical state shows that it is possible to discriminate features with changes of pressure and/or temperature. Some of the data were acquired with a rather large pressure uncertainty considering the phase diagram and the large heat capacity variations (see the different figures at the beginning of this report especially figures 3, figures 6 to 8). Even with the preceding restrictions, it can be concluded that the size of the vapour-like and liquid-like domains seems to be different and that the ILL set up is able to give accurate and valuable data for a complete understanding of that P and T region compared to higher pressure and higher temperature.

Future actions and experiments/proposals to be planned:

In order to have a higher level of stability for both T and P, and a better control in the experimental cell. It is planned to interact with the Technical ILL Service for building a new experimental set-up with the ability to inject different compounds in the SC fluid (2 gases in the SC state / 1 gas and a co-solvent / 1 gas + 1 co-solvent and a third body).

It is planned to launch several actions, they are

- to complete the first series of diffraction data by a second series of experiments,
- to proposed thesis topics about understanding the CO_2 supercritical state and about obtaining related data for further technological applications in the frame of the recent call for proposals in the frame of “InnovaXN PhD projects at ILL/ESRF”.