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Experiment Report

Proposal SC-5158
"Influence of high pressure on the supramolecular structures in alcohols"
Beamline: ID15B
Beam time allocated: 18 shifts
Beam time used: 18 shifts
Start-finish date: 07/12/2021-13/12/2021
Beamline scientists: Michael Hanfland

The aim of the experiment was to measure the X-ray diffraction for a series of alcohols as well as pharmaceuticals differing in the molecular structure under high pressure up to GPa level. The selected materials are compounds forming supramolecular assemblies and organization of molecules on the medium-range scale. The ordering of the molecules can be treated as a phase intermediate between crystalline and amorphous. The interactions causing such a structuring in the studied materials are generally hydrogen bonds and van der Waals forces. ESRF was necessary for this experiment since ID15B beamline enables extremely unique diffraction measurements of liquid samples under high pressure up to the level of GPa, in a wide range of q starting from ~0.3 $Å^{-1}$ that is crucial for studying the supramolecular structures and nanoscale ordering.

We measured the samples at different temperature and pressure conditions using the diamond-anvil cell (DAC) technique. Our previous dielectric spectroscopy measurements under high pressure indicated for most of the studied compounds what are the glass transition pressures depending on the temperature. Therefore, we were able to predict what is the region of the liquid state on the phase diagram for the studied samples. Therefore, the samples were measured as liquid up to around the glass transition pressure for a given temperature. In the proposal we submitted the following substances for measurements:

1) 2-ethyl-1-hexanol,
2) 2-ethyl-1-hexylamine,
3) butyl alcohol (n-butanol),
4) 4-phenyl-1-butanol,
5) 4-cyclohexyl-1-butanol,
6) 1-propanol (n-propanol),
7) 3-chloro-1-propanol,

8) 3-bromo-1-propanol,
9) 3-iodo-1-propanol,
10) ritonavir,
11) felodipine,

All the substances were packed in DACs and measured under required temperature and pressure conditions. We think that we managed to perform more than three-quarters the intended measurement program. We appreciate the course of the experiment and the help of beamline scientists very well.

As a results of the measurements we got scattering intensity functions versus the scattering vector in the range around 0.5-30° in the 2Theta scale (0.15-8 $Å^{-1}$ in the scattering vector scale). Due to strong absorption of X-ray by the DAC, also empty DACs were measured. The background scattering from the empty cell was then properly subtracted. The data were corrected for measurements artefacts such as diffraction from diamonds and for background including the changes in the intensity due to X-ray beam fluctuations with the time of the measurements. The selected diffraction data collected during the experiment are shown below:

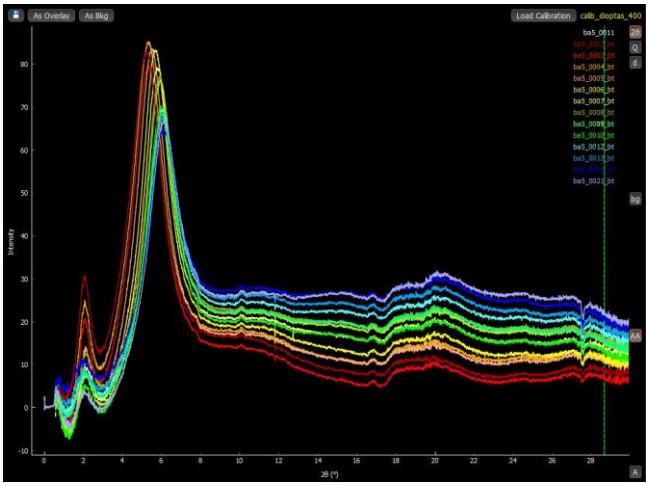

Fig. 1. The obtained diffraction data for 2-ethyl-1-hexanol at 295 K as a function of pressure up to around 3.12 GPa.

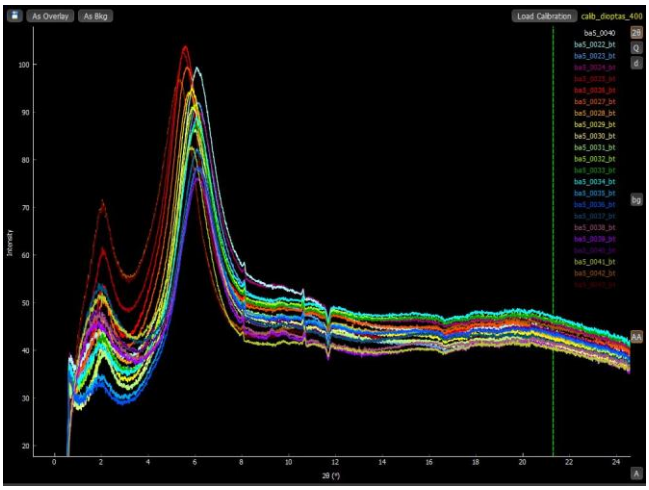

Fig. 2. The obtained diffraction data for 2-ethyl-1-hexanol at 323 K as a function of pressure up to around 3.75 GPa.

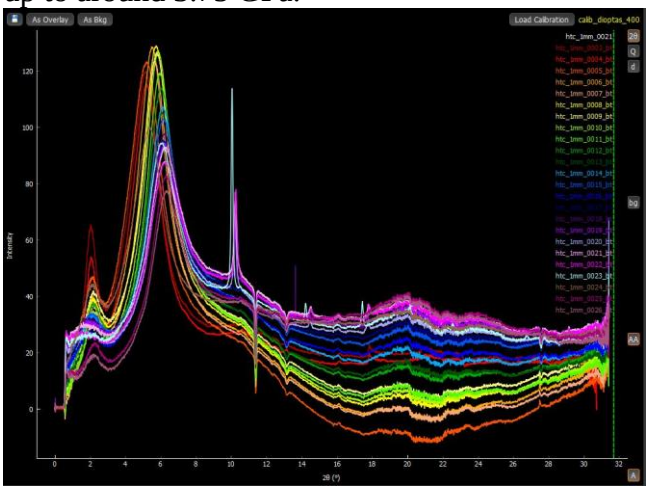

Fig. 3. The obtained diffraction data for 2-ethyl-1-hexanol at 373 K as a function of pressure up to around 5.8 GPa.

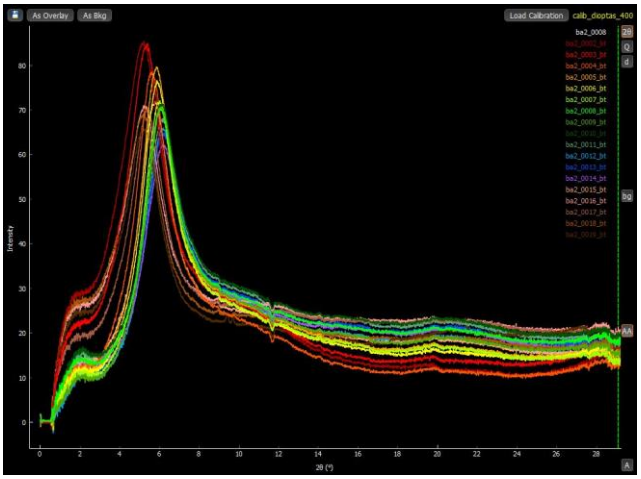

Fig. 4. The obtained diffraction data for 2-ethyl-1-hexylamine at 295 K as a function of pressure up to around 3.9 GPa.

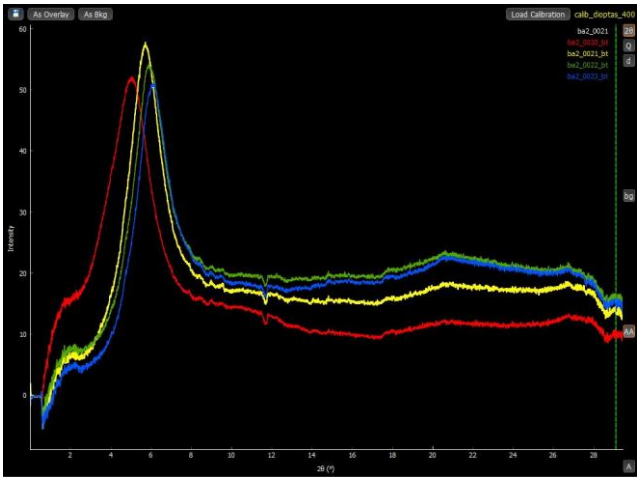

Fig. 5. The obtained diffraction data for 2-ethyl-1-hexylamine at 323 K as a function of pressure up to around 3.9 GPa.

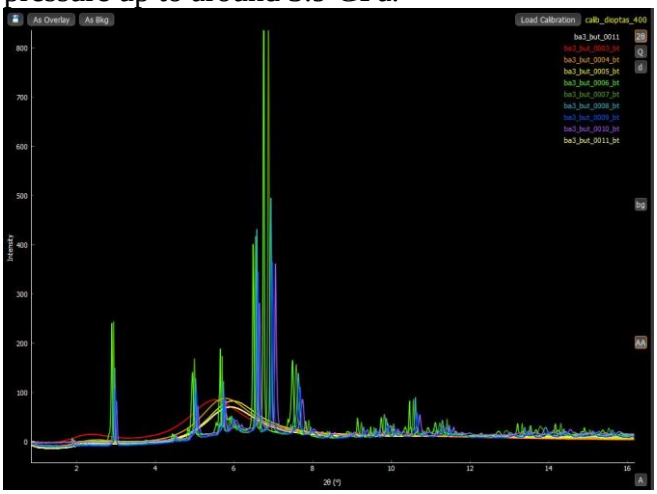

Fig. 6. The obtained diffraction data for 1-butanol at 298 K as a function of pressure up to around 3.5 GPa. The crystallization of sample around 1.5 GPa is visible.

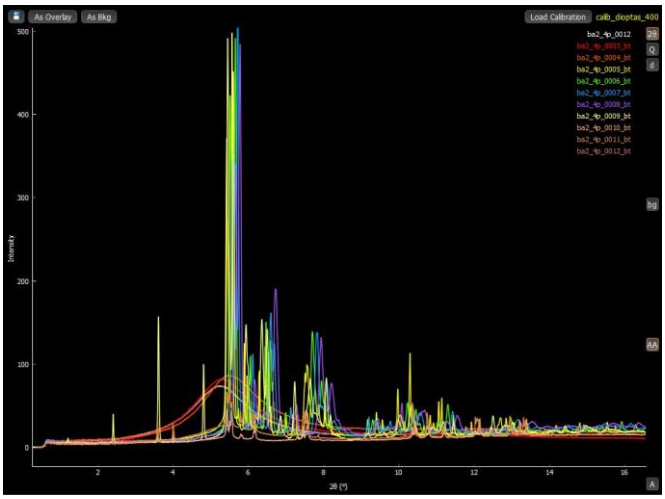

Fig. 7. The obtained diffraction data for 4-phenyl-1-butanol at 298 K as a function of pressure up to around 4.0 GPa. The crystallization of sample around 1.0 GPa is visible.

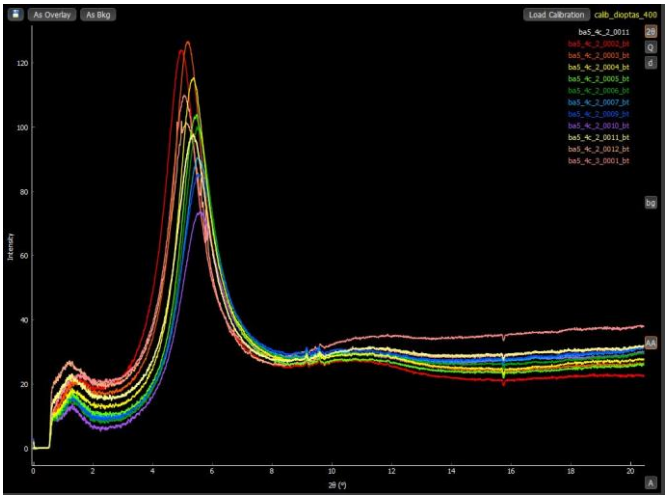

Fig. 8. The obtained diffraction data for 4-cyclohexyl-1-butanol at 298 K as a function of pressure up to around 4.0 GPa.

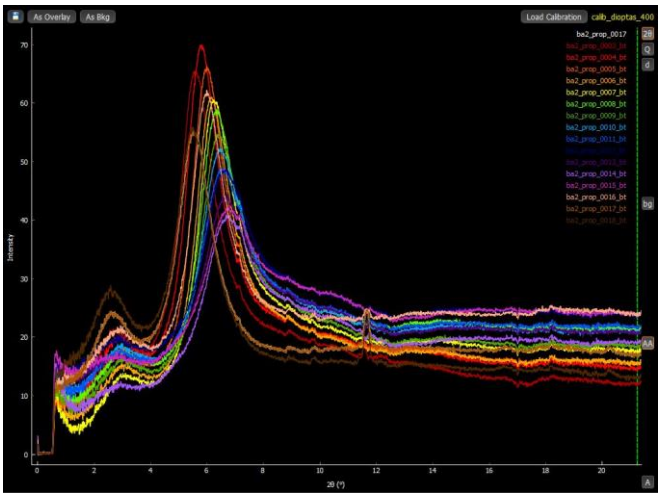

Fig. 9. The obtained diffraction data for 1-propanol at 298 K as a function of pressure up to around 6.0 GPa.

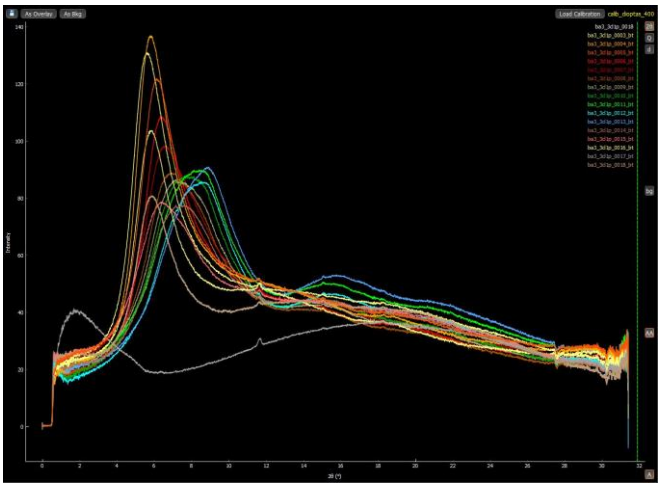

Fig. 10. The obtained diffraction data for 3-chloro-1-propanol at 298 K as a function of pressure up to around 6.0 GPa.

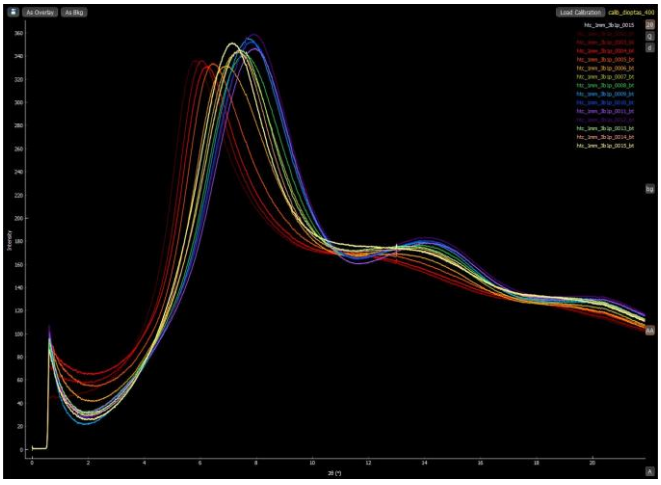

Fig. 11. The obtained diffraction data for 3-bromo-1-propanol at 298 K as a function of pressure up to around 3.5 GPa.

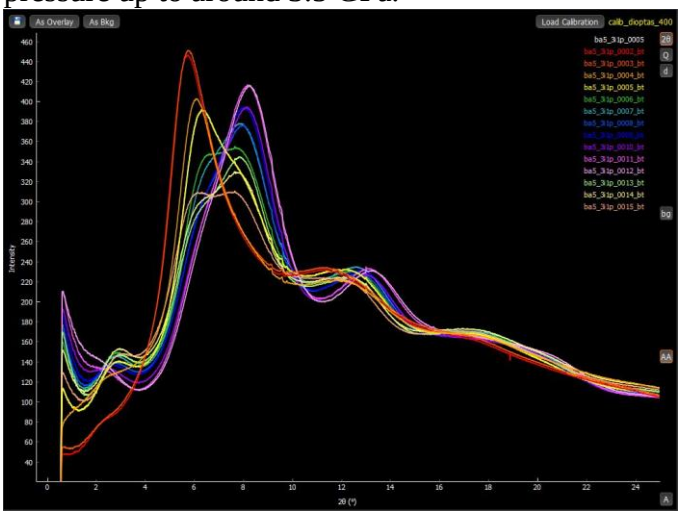

Fig. 12. The obtained diffraction data for 3-iodo-1-propanol at 298 K as a function of pressure up to around 6.0 GPa.

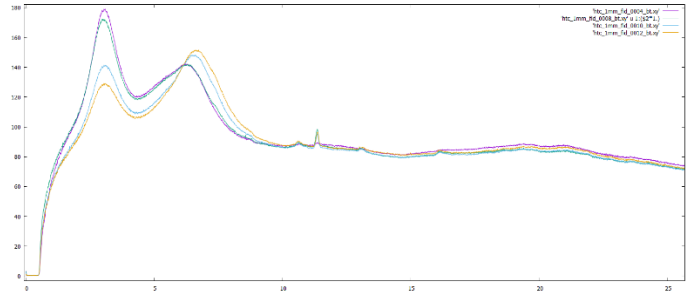

Fig. 13. The obtained diffraction data for felodipine as a function of pressure up to around 0.5 GPa.

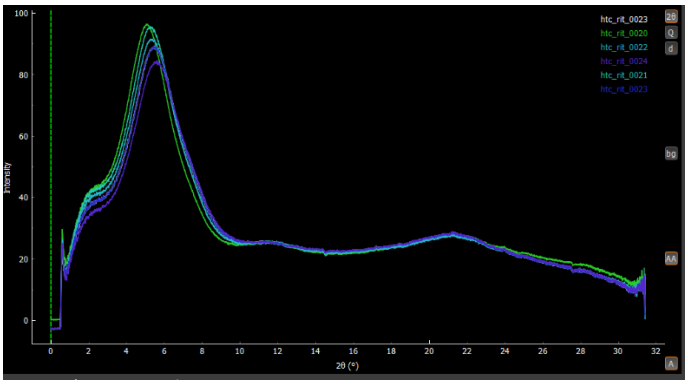

Fig. 14. The obtained diffraction data for ritonavir as a function of pressure up to around 2.0 GPa.

The obtained data will be analyzed in terms of the properties of the main diffraction peak and the pre-peak at the low scattering vector range. The pre-peak is a fingerprint of the

medium range ordering of the molecules. The experimental data will be set together with the data of dielectric spectroscopy measured under high pressure at our group at the University of Silesia as well as with the results of the molecular dynamics simulations under high pressure. The results help to understand how different features of the molecular structure and intermolecular interactions behave under high pressure that is fundamental knowledge crucial for the explanation of the properties of the matter under various thermodynamic conditions.

We hope, the results of this experiment will be published in journals with good impact factors.