

## Local structures in supercritical solutions: an in situ investigation by X-ray synchrotron radiation

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### Introduction

The understanding of the processes of molecular interactions in fluids at elevated pressures and temperatures is of crucial importance, in particular in the case of aqueous solutions. The growing interest in these processes stems from both fundamental and applied insights, that their understanding brings to the geochemical, biochemical, and industrial communities. It must be emphasized in the case of aqueous solutions that the interparticle interactions under elevated temperature and pressure conditions are very sensitive to the structure of the solvent and, in particular, to the hydrogen bonding strength. As a consequence, studying the structural and electronic evolution of solute particles in aqueous solutions is an efficient indirect method to get information on the solvent itself [1,2].

### Methods and Materials

In this framework, a new line of research has been initiated five years ago in the laboratory of crystallography (CNRS, Grenoble). It consists of understanding the relation between physical properties and structural organization of liquids under elevated conditions of pressure and temperature, up to and beyond their critical point. Such a challenging program is now made possible by the availability of the extremely bright and well focused X-ray beams at ESRF, combined with our expertise in the design of high temperature and high pressure cells [3]. We devoted our recent efforts to the determination of the molecular structure of hydration of ions and molecules in supercritical water and aqueous solutions by X-Ray Absorption Spectroscopy (on FAME and ID26 XAS endstations), X-Ray Raman Inelastic Scattering [4] and Small Angle X-Ray Scattering [5-7] to determine the structure of the mesoscopic inhomogeneous distribution of water molecules in the compressible regime.

A new optical high pressure/high temperature (HP/HT) cells design for independent 1-2000 bar and 30-1700°C variations (fig. 1) developed for fluorescence spectroscopic studies is presented.

From a geochemical and geophysical point of view, the pressure range of our instruments is very well adapted for in situ studies of hydrothermal fluids, sub- and supercritical natural solutions. This range is complementary to the great pressures obtained with Paris-Edinburgh (PE) presses or Diamond Anvil Cells (DAC), necessary to investigate the pressure issues in the mantle crust science.

These cells are dedicated to X-Ray Absorption Spectroscopy, Small Angle X-Ray Scattering, Inelastic X-Ray Scattering and Visible Raman Scattering techniques. It allows the study of aqueous solutions (T<600°C and P<100 bar) and liquid metals and glasses (T<1700°C and P<2000 bar). The precision in the

measurement of pressure is around 1 bar, around 1° for the temperature.

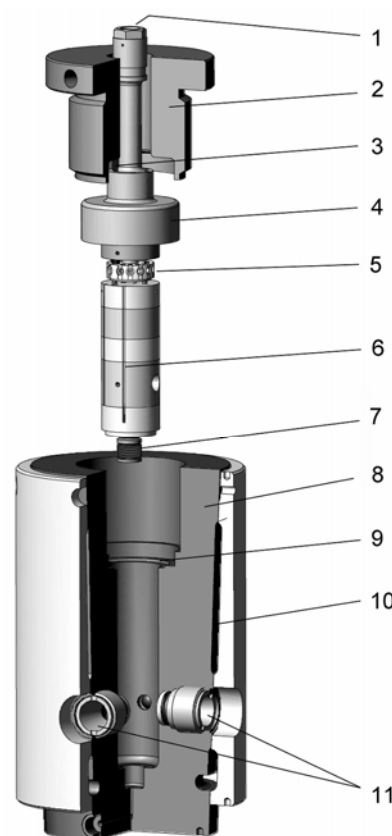


Fig. 1: 3D drawing of the hp-ht setup: the diameter of the HP vessel (8) is 150 mm. (1) He inlet through the HP vessel plug, (2) HP vessel nut to hold tight the vessel plug, (3) pyrophyllite leadthroughs, (4) HP vessel plug, (5) thermocouples and electrical leads connections to the internal part, (6) thermocouple, (7) bellows on the internal cell, (8) HP vessel, (9) viton seal, (10) water cooling circulation, (11) thin Beryllium windows

The technology of our set-up is based on helium pressurization of the vessel in which the sample and its heating system are located. Different sample container configurations exist, depending on the used techniques, on the investigated samples and on the conditions of temperature and pressure. A dedicated cell can be mounted for aqueous samples, allowing an easy and precise prospection of the (P,T) phase diagram. Original HP windows have been developed with a large 22° angular opening.

This experimental set-up is especially suitable for *in situ* experiments, for kinetic studies... Moreover, the design of the cells always allows the measurement of the

transmitted signal. The density of the sample versus the (P,T) conditions can be then systematically measured during the other acquisition (fluo-XAS, SAXS...). This macroscopic information is very useful to follow either a precipitation or a dissolution process.

## Results

The obtained results allow to probe the structure of the supercritical system at different scales. XAS [2,3,4] and XRIS [5] studies have allowed to establish the molecular structure of hydration of ions and molecules in water and the unique structure of hydrogen bonding in pure supercritical water. In the mesoscopic range, the determination of inhomogeneous distribution of water molecules in the compressible regime has been determined by SAXS [6].

The presented XAS results show variations in the number, nature and distance of neighbors around both cations and anions in water as a function of temperature, pressure and concentration. In the following, we relate these changes to the water solvent properties. In non-critical (P,T) conditions, an increase of both temperature and concentration produces an increase of ion pair formation. The formation of ion pairs is accompanied by a dehydration around ions. On the contrary, an increase of pressure produces a decrease of the number of ion pairs. The ion-pair formation is driven by Coulomb forces between ions and by interactions between the ions and solvent polar molecules. A significant parameter allowing to understand the evolution of ion-pair formation is the dielectric constant. In the classical frame of the electrostatic description of dielectric media, the Kirkwood theory yields an analytical expression of  $\epsilon$  in the case of a polar solvent with H-bonding. In liquid water, the dipole correlation mediated by H-bonding gives rise to an extended network of H-bond based on a tetrahedral local order. In non-critical conditions, our results can simply be interpreted. An increase of concentration brings the ions closer to each other and thus increases the strength of the Coulomb interaction, favoring ion pairing.

From normal to supercritical (P,T) conditions, there is a strong decrease of  $\epsilon$  values due to an increase of  $T$ . There is also probably a variation of the dipole moment. The structure of water itself is affected; the number of H-bonds strongly decreases and there is a destruction of the extended H-bond network at rather low temperature (~416 K). The pair distance variation observed with increasing temperature up to the supercritical region (contraction of cation-O and cation-anion distances, between normal and high  $P$ ,  $T$  conditions while the anion-O distance remains about constant) can be understood with respect to the variation of  $\epsilon$  values.

Small Angle X-Ray Scattering (SAXS) studies determine the structure of the mesoscopic (tens of angstroms) inhomogeneous distribution of water molecules in the compressible regime.

The present SAXS results permit to describe the structure of the density fluctuations that appear at high temperature and high pressure. They are a common characteristic of

all fluids and can be basically described as the coexistence of dynamical dense clusters of solvent molecules in low density regions. SAXS experiments combined with an Ornstein Zernike analysis leads to the determination of the correlation length  $\xi$  and the compressibility  $\chi_T$  of the fluid. From these SAXS studies and previous X-Ray Absorption Spectroscopy works [2,3] we proposed [6] a sequence for particles interactions at HT/HP conditions:

- 1) from ambient to about 300°C, the increase of temperature results in a decrease of the dielectric constant  $\epsilon$  of the solvent leading to ion pairing by coulombic attraction
- 2) above 300°C, the onset of density fluctuations that develop from the local ions hydration shells results in an enhanced screening effect between ions which stops the ion pairing.

In a last part, we report a study done at 380°C/300 bar (density around 0.54 g/cm<sup>3</sup>). As indicated above, supercritical conditions like this are characterized by the existence of high density clusters of water molecules surrounded by a low density (gas-like) medium. The RIXS experiment allowed for the first time a molecular description of the local hydration of the water molecules in these high density clusters: the number of hydrogen bonds is larger than in ambient water, but the bonds are more distorted. By considering SAXS results obtained at the same supercritical conditions [5], the XRIS results lead also to the quantitative determination of the ratio of each water molecule species (molecule without hydrogen bond, molecule with hydrogen bond).

## Acknowledgements

We thank all the people who participate to this extended work, through a strong collaboration or for their important help before or during the experiments.

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