ESRF	**Experiment title: XAS Study of highly diluted $ZnBr_2$ in supercritical fluids (H_2O, methanol, ethyl acetate)**	**Experiment number**: 30.02.682
Beamline: BM30b	**Date of experiment**: from: 10/06/2004 to: 17/06/2004	**Date of report**: 15/10/2004
Shifts: **18**	**Local contact(s)**: Hazemann Jean-Louis	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Proux Olivier, CNRS - Laboratoire de Géophysique Interne et Tectonophysique, Grenoble

*Testemale Denis, Swiss Norvegian BeamLine

*Hazemann Jean-Louis, CNRS - Laboratoire de Cristallographie, Grenoble

Experimental details.

High pressure / high temperature XAFS spectroscopy analysis of $ZnBr_2$ solutions were performed at Br K-edge, using an X-ray cell recently developed at the Laboratoire de Cristallographie (Grenoble) [1]. This cell allows simultaneous measurement of the absolute concentration of the absorbing element in the fluid (from edge-step height in transmission mode), and the determination of the atomic environment around the absorber (from analysis of XANES and EXAFS spectra in fluorescence mode). The $ZnBr_2$ concentration was 0.033mol/l for the water solution, 0.085 and 0.0085mol/l for the methanol solutions.

$ZnBr_2$ aqueous solution

The comparison of the obtained EXAFS oscillations (figure 1) and those from the previous experiments [2,3] clearly shows that:

- Br ions are largely hydrated under normal conditions (max. of the oscillations for low k values at ~2.5 $Å^{-1}$)
- ions pairs are formed in hydrothermal conditions (max. of the oscillations for medium k values at ~6 $Å^{-1}$)

Previous results obtained on $ZnBr_2$ aqueous solutions have shown that ion pair formation start around 125°C for a 0.17mol/l concentration [3]. For a 5 times lower concentration, this evolution appears between 200 and 300°C.

$ZnBr_2$ methanol solution

The evolutions of the edge heights (figure 2) are similar for temperature lower than 150°C. For the 0.0085mol/l concentration, the normalized edge heights seems to follow the pure methanol density, the drop of the height around 250°C might be linked to the strong decrease of the methanol density in this temperature range (no data was found for pure methanol in the supercritical area but $?_c$=0.273g/cm^3 at 78.5 bars and 239.6°C). For the 0.085mol/l concentration, the decrease of the edge heights appears around 200°C; this might be due to the deposition of solid salts out of the beam path as result of precipitation.

The comparison of the modulus of the Fourier Transform of the EXAFS oscillations (figure 3) are similar for both concentrations. The only evolution is a decrease of the intensity of the FT *vs* temperature, simply due to the increase of the thermal disorder. Contrarily to the aqueous case, it seems that no ion-pairing occurs in the $ZnBr_2$ methanol solution.

Conclusion and perspectives

The main objective of this experiment was to study very diluted solutions, in order to get rid of any clustering effect at ambient conditions and thus be sensitive only to the evolution of ion pairing. The very good quality of the data shows the feasibility of such XAS measurements. Precise simulations are under progress in order to quantify these effects and to understand why a precipitation seems to occur (from the edge height evolution) until no ion pairs are clearly seen on the EXAFS data.

The goal of our future experiments will be to study the $ZnBr_2$ methanol solution at the Zn K-edge and $ZnBr_2$ salt in a non-polar solvent (ethyl acetate).

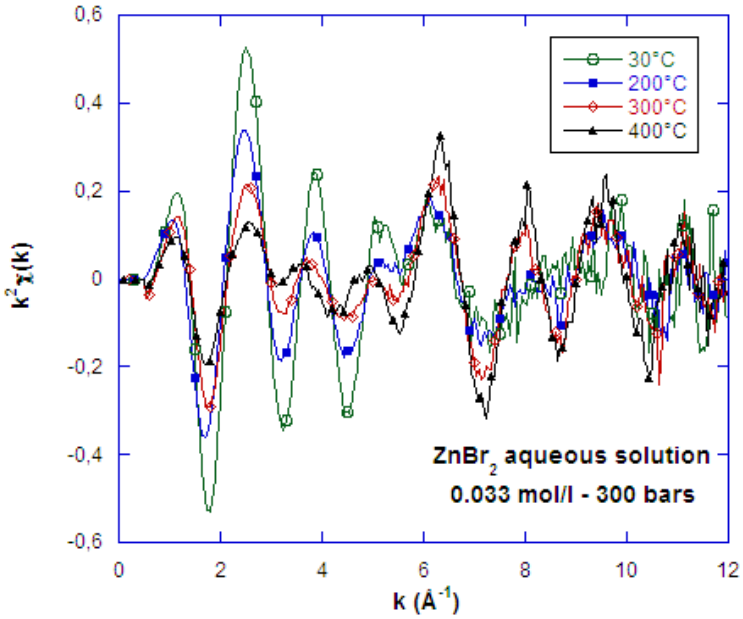

Figure 1 : k^2?(k) EXAFS signals obtained at the Br K-edge in the fluorescence mode for the $ZnBr_2$ aqueous solution (concentration: 0.033 mol/l) at different temperatures (pressure: 300 bars).

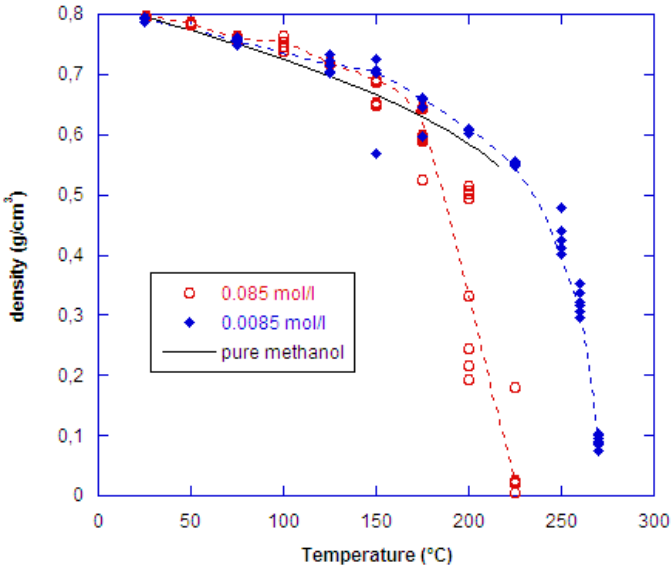

Figure 2: Absorption edge heights measured in the transmission mode for the $ZnBr_2$ methanol solutions at the Br edge, for two concentrations, 0.085 and 0.0085 mol/l, *vs* temperature (pressure: 100 bars). Heights have been normalized to pure methanol density at 25°C and are then compared to the solvent density (solid line).

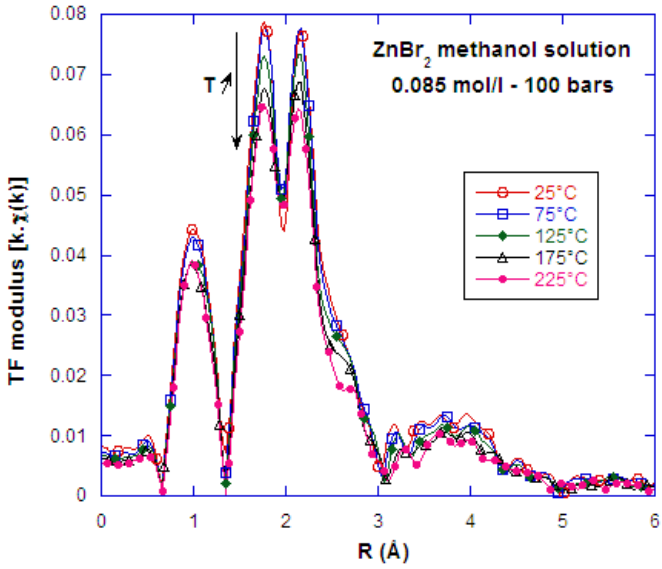

Fig. 3 : modulus of the k?(k) Fourier Transform signals obtained at the Br K-edge in the fluorescence mode for the $ZnBr_2$ methanol solution (concentration: 0.085 mol/l) at different temperatures (pressure: 100 bars).

References

[1] Argoud R. *et al.* "High pressure / high temperature cells for in situ structural investigations in geothermal conditions", *proceedings of the Réunion des Sciences de la Terre, Strasbourg* (2004)

[2] Simonet V. *et al.* "X-ray absorption spectroscopy studies of ionic association in aqueous solutions of zinc bromide from normal to critical conditions", *J. Chem. Phys.*, **117** (2002) 2771-2781

[3] Simonet V. *et al.* "Structure of aqueous ZnBr2 solution probed by X-ray absorption in normal and hydrothermal conditions", *J. Chem. Phys.*, **116** (2002) 2997-3006