ESRF	**Experiment title:** Structural changes of water-NaOH and water-HCl solutions at high pressure and high temperature	**Experiment number**: CH-3900
Beamline: ID20	**Date of experiment**: from: 29 Jan 2014 to: 04 Feb 2014	**Date of report**: 29.09.2014
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Report: The purpose of the experiment CH-3900 was to study the changes in the local atomic environment of the oxygen atoms in aqueous solutions of sodium hydroxide and hydrogen chloride under simultaneous high temperature and high pressure conditions.

The question about the local atomic structure of these solutions is of fundamental interest and may lead to a deeper understanding of the influence of charged particles on the hydrogen bond network of water [Botti04a, Botti04b]. Furthermore, aqueous solutions of NaOH and HCl at elevated T and p are highly relevant in the chemical industry and, in particular, solutions of HCl in geological processes such as the formation of hydrothermal ore deposits [Reed97], geothermal systems, and volcanic fumaroles.

The high temperature and high pressure conditions necessary for this study were achieved using a resistively heated hydrothermal diamond anvil cell (HDAC). This equipment was used at ID16 before [Sahle13] and was now used at the new beamline ID20 for the first time. The pressure was determined from the liquid-vapor homogenization temperature before and after the experiment, the composition, and the equation of state [Wagner02] or correlation formulae for phase relations [Schmidt07].

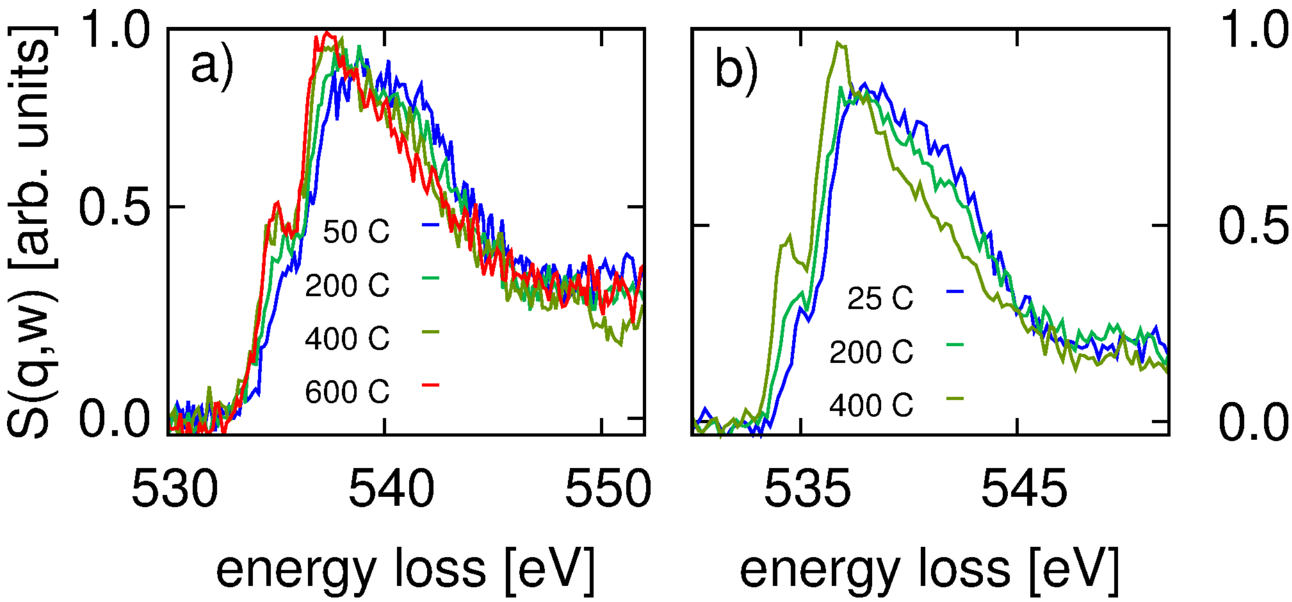

Figure 1: a) Results of the current experiment: O K-edge spectra of aqueous 34 m.% NaOH solutions for different temperatures and pressures. b) Results of a previous experiment: O K-edges from 14 m.% aqueous solutions of HCl.

Figure 1 a) shows the results of a series of oxygen K-edge spectra for a 34 mass. % aqueous solution of NaOH at a series of temperatures and pressures. Figure 1 b) shows data from an earlier experiment (HE-3591) of a 14 mass. % aqueous HCl solutions for similar temperatures and pressures.

For both, NaOH and HCl, we find a systematic changes of the oxygen K-edge as a function of T and p: a sharpening of the pre-edge feature around 535.5 eV energy loss and a loss of spectral weight in the post-edge region aroung 540.0 eV energy loss. However, even though the NaOH solution was measured at a much higher concentration (34 mass % Na vs. 14 mass % HCl), the changes in the oxygen K-edge of the NaOH solution are much more subtle indicating a different influence of OH- ion and protons on the hydrogen bond network at extreme conditions.

The data analysis is still in progress. We are currently developing atomic structure models from ab initio molecular dynamics simulations and spectra calculations will then be performed based on the Bethe-Salpether equation using the new OCEAN software [Vinson11]. With these computational tools we hope to get a deeper insight into the microscopic changes of the hydrogen bond network of water under extreme conditions upon addition of charged particles.

[Botti04a] A. Botti et al. (2004) Ions in water: The microscopic structure of concentrated NaOH solutions. J. Chem. Phys. 120, 10154-10162. **[Botti04b]** A. Botti et al. (2004) Ions in water: The microscopic structure of a concentrated HCl solution. J. Chem. Phys. 121, 7840-7848. **[Reed97]** M.H. Reed (1997) Hydrothermal alteration and its relationship to ore fluid composition. In Barnes, H.L. (Ed.) Geochemistry of Hydrothermal Ore Deposits, Wiley, pp. 303-366. **[Sahle13]** Sahle Ch.J. et al. (2013) Microscopic structure of water at elevated pressures and temperatures. PNAS 110, 6301-6306. **[Wagner02]** Wagner W., Pruß A., J. Phys. Chem. Ref. Data 31, 387–535 (2002). **[Schmidt07]** Schmidt C., Rickers K., Bilderback D.H., Huang R., Lithos 95, 87–102 (2007). **[Vinson11]** J. Vinson et al. (2011) Bethe-Salpeter equation calculations of core excitation spectra. Phys. Rev. B 83, 115106.